Characteristics and Applications of High-Silicon Aluminium Alloys

Important Developments in Applications

Alloys of aluminium and silicon are of great industrial importance; those containing from 3% to 12·5% of silicon are especially well-known to producers and users of light metal castings, but this article is concerned mainly with the 10% to 12·5% silicon-aluminium alloys and with developments in their application.

THE silicon aluminium series of alloys, with an alloying content ranging up to 12·5% of silicon, has, for many years, been widely employed on a commercial industrial scale. Generally speaking, those alloys containing up to 1% of silicon belong to the wrought alloy class, the alloying addition usually being employed in conjunction with magnesium to confer heat treatability on the material, whilst those containing from 3% to 12·5% of silicon belong, with but few important exceptions, to the casting alloy group.

With regard to the alloys of maximum silicon content (of the order of 10% to 12·5%) with which this article is principally concerned, it is now well recognised that the chief spheres of utilisation lie in the direction of large sand and/or die-castings for marine and general engineering work. Alloys belonging to this type are now employed in the form of sand or gravity die-castings alloys for purposes such as turbine gear casings, radiators, parts of pumps, gear box casings and housings of various types. They are characterised by high corrosion resistance, good foundry characteristics, low specific gravity, and high ductility and impact strength.

The inclusion of small percentages of manganese and magnesium in casting alloys of this type renders them amenable to heat-treatment, with consequent improvement of mechanical properties. When maximum mechanical properties are desired, however, such alloys must be subjected to a special "modification" process. The mechanism of such modification has been for long a matter of extreme interest to metallurgists and is still the subject of intensive investigation.

Under ordinary conditions, an alloy containing 11% to 12% of silicon solidifies in the eutectic form at 578° C., but when modified by treatment with metallic sodium or alkaline fluorides, the eutectic moves up to 14% of silicon with a solidifying temperature of 564° C. Micro-examination reveals that the improvement of mechanical properties is due primarily to a refinement of the grain structure.

Oil sprayer cover for turbine gear casing cast in 12·5% silicon aluminium alloy to Admiralty Specification DNC/M/IC

The Daimler Benz DB 600 engine with crankcase cast in one part in Silumin Gamma alloy.
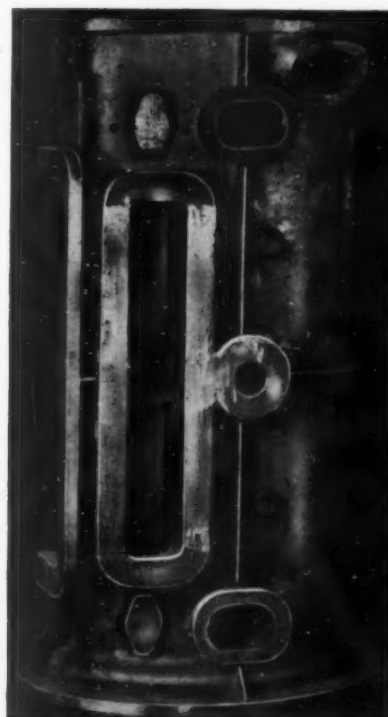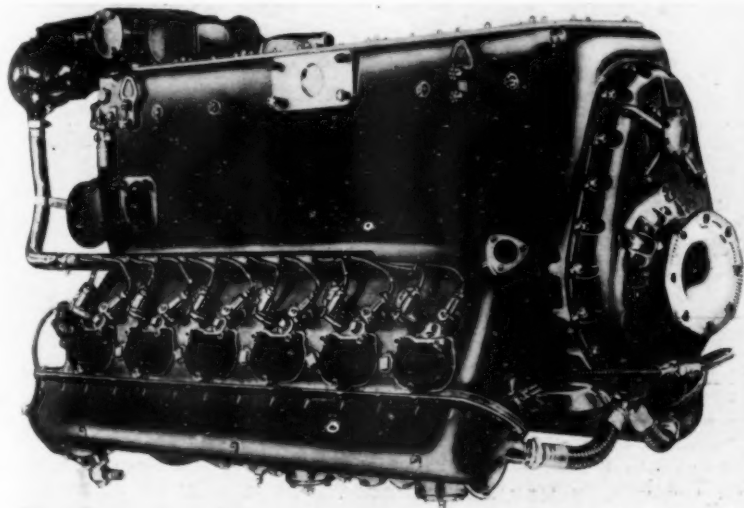
The method generally followed in carrying out modification is as follows : Approximately 0·1% of modifying metal, usually sodium, is added to the molten metal, maintained within ± 30° of 750° C., the sodium being wrapped in aluminium foil and plunged into the melt in a perforated inverted crucible similar to that used for the addition of magnesium. An important requirement is that the correct time should elapse between modification and casting. If the time is insufficient a blue metallic film forms after skimming, whilst if the interval is too long the modification effect disappears, the metal being said to have " reverted." A characteristic of incompletely modified metal is, of course, unduly large grain growth.

It has been pointed out by various authorities that gas content or treatment by gas has a marked effect on modification, this depending on whether the composition of the alloy lies above or below the eutectic point. In the latter case, some modification generally occurs as a result of chlorine treatment, but if the composition lies above the eutectic point, the reverse applies, the grain structure being very much coarsened.

When modification by sodium or sodium salts is followed by treatment with chlorine gas, rapid demodification takes place, and if gassing be continued, the alloy will ultimately revert to a coarse-grained structure. Also, if a degassed alloy be subsequently treated with sodium a considerable amount of gas appears to be put back into the melt. The reason for this is still a subject of intensive research.

Alloys of the type under review have been extensively developed, both in this country and in Germany. The relevant British specifications are DTD 240, covering Alpax Beta, N.A. 161/A3 and Wilmil (HT) ; and DTD 245, relating to Alpax Gamma, N.A. 161/T.68, B.A. 40/N and Wilmil M (fully heat-treated). The former specification lays down a partial heat treatment— at 150° to 170°C for not less than 16 hours, cooling being carried out in air or by an oil or water quench—whilst DTD 245 specifies full heat treatment. This involves heating at 520° to 535° C. for two to four hours and quenching in cold water, followed by reheating at 150° to 170° C. for not less than 16 hours after which the material is cooled as specified in DTD 240. Chemical compositions and mechanical properties indicated in the relevant specifications are set down in Table I.

TABLE I.

D.T.D.	Chemical Compositions					Mechanical Properties					
	Mn.	Mg.	Si.	Fe.	Other Elements	0·1% Proof Strength		Ultimate Tensile Strength		Elongation %	
						Test Bar	Chill Cast	Test Bar	Chill Cast	Test Bar	Chill Cast
240	0·6	0·6	10–13	0·6	0·2	6	8·5	11	15	1·5	3·0
245	0·6	0·6	10–13	0·6	0·2	13	16	15·5	19		

Alloys of a similar type have found wide application as piston materials, a considerable advantage possessed by them being the property of relatively low expansivity. An alloy of the composition indicated in Table II. possesses, in addition to a low co-efficient of thermal expansion, high mechanical strength at elevated temperatures, good casting and die-casting properties, excellent bearing properties and the capacity to form an anodic film which readily absorbs an " oily " lubricant film. This material is being used for pistons, ranging in size from the smallest petrol engine type to compression ignition engine pistons up to 20 ins. in diameter.

TABLE II.

Chemical Composition of Piston Alloy %				
Si.	Cu.	Mg.	Ni.	Fe.
12·0	0·8	1·0	2·5	0·8

So important has this casting-material proved for piston construction that a wrought alloy, of similar constitution and mechanical and physical characteristics, has been developed for aircraft engine pistons and cylinder barrels. This alloy is covered by DTD Specification 324, the chemical composition and mechanical properties laid down being shown in Table III.

TABLE III.
Characteristics of Wrought Piston Alloy of High Silicon Content.

Chemical Composition					Mechanical Properties	
Cu.	Mg.	Si.	Ni.	Other Elements	Ultimate Tensile Strength Tons/Sq. in.	Elongation % on 2 ins.
0·7–1·3	0·8–1·5	11·5–13·5	0·7–1·3	0·6	20	3

In Germany, alloys of the high-silicon type, known as Silumin, have also been developed intensively, typical chemical compositions being shown in Table IV.

TABLE IV.

Silumin Alloys	Chemical Compositions %		
Silumin	13·0	—	—
Silumin Beta	13·0	0·17	0·5
Silumin Gamma	13·0	0·17	0·5

Fe.—0·6 max. ; Tu.—0·2 max. ; Cu.—0·1 max. ; Ti.—0·1 max.

The materials are used widely in the sand or die-cast form, to which fact reference will be made later, but considerable interest attaches to the fact that Vereinigte Leichmetall-Werke G.m.b.H., of Hanover, have, for some time, been producing the alloys in the rolled and extruded forms. The mechanical properties obtained with the materials in various rolled conditions are given Table in V.

TABLE V.
Mechanical Properties of Rolled Silumin Alloys.

Condition of Alloy	Mechanical Properties.			
	Tensile Strength lb./in² ×10³	Proof Stress lb./in² ×10³	Elong. %	Brinell Hardness Kg. per Sq. mm.
31W Annealed	17—22	9—12	15—25	40—50
31H½ Half Hard	22—29	17—22	3—10	50—60
31H Hard	26—36	22—29	2— 5	60—80
31P as extruded	14—22	12—14	10—18	40—55

Probably the most interesting German application for the casting alloy, however, is in the construction of the crankcase of the Daimler Benz " DB600 " engine. This power unit, which is incorporated in Messerschmitt, Heinkel and Dornier aircraft now used by the Luftwaffe, is a liquid-cooled, 12-cylinder (inverted) " V " engine, which develops 1,050 b.h.p. for starting, with a nominal output of 1,000 h.p. and 800 h.p. continuous output. The crankcase is cast in one part in Silumin Gamma, being braced by ribs and transverse partitions and closed at the top by a lid.

Silumin Gamma is used extensively for a similar purpose in other German aircraft and automobile engines and for cylinder heads of water-cooled engines. In connection with this last mentioned application, the addition of cobalt or manganese has been found to be beneficial in increasing the fatigue limits slightly without impairing the good casting qualities of the original alloy.

The Spekker Steeloscope and Photo-electric Absorptiometer.

Some time ago we notified readers that Messrs. Adam Hilger, Ltd., had appointed Wild-Barfield Electric Furnaces, Ltd., sole distributors in the United Kingdom of the Spekker Steeloscope. These arrangements have now been extended, and include the Spekker Photoelectric Absorptiometer. This latter instrument provides a rapid, yet accurate, means for quantitative analysis of practically all metals by colorimetric methods. It possesses several advantages over visual colorimeters, the more important being that measurements are entirely independent of the visual judgment of the observer, while, except for initial calibration of the instrument, no standard solutions are necessary.

American Society for Testing Materials

44th Annual Meeting at Chicago

A STRONG technical programme was arranged in connection with this annual meeting held on June 23–27, a prominent feature of which was a Symposium on Problems and Practices in Determining Steam Purity by Conductivity Methods, comprising six papers. Two separate technical sessions were necessary to cover the field of non-ferrous metals. Because of national defence consideratious, the importance of many of the problems covered in these sessions is without parallel in previous years. Other important sessions covered plastics, steel and effect of temperature, fatigue of metals and corrosion of iron and steel.

Non-ferrous Metals

In addition to several Committee reports, many papers were presented dealing with developments in particular fields. The properties of certain lead-bearing alloys, for instance, were considered by A. J. Phillips, A. A. Smith, Jr., and P. A. Beck, in which the authors deal with a lead-base alloy containing approximately 12·5% antimony, 3% arsenic, and 0·75% tin, and compare it with conventional lead- and tin-base alloys. It is shown that at elevated temperatures the new alloy has outstanding properties which are retained after prolonged periods of heating, whereas the standard alloys show considerable softening under such conditions. The new alloy is easy to cast, retains its composition with repeated remelting, and is ductile enough at elevated temperatures to permit shaping. The liquidus temperature is 295° C. and the solidus 242·5° C.

In the lamp and radio industry, fine wire sizes are expressed in terms of weight per unit length requiring accurate data on density at fine sizes. In a paper by S. Umbreit, a technique is given which is suitable for determining the density of wire from 0·001 to 0·010 in. in diameter, using specimens as small as 1 grm. with a constancy of about ± 0·05%. Determinations on nickel alloys, molybdenum, tantalum, tungsten, and platinum alloys are reported on wires about 0·001 in. and 0·003 in. in diameter.

Dezincification of alpha brasses is considered in a paper by W. Lynes in relation to (1) proper choice of an inhibitor, and (2) evaluation of possible detrimental effects of the inhibitors commonly used. As a basis for the conclusions presented, relevant published and unpublished information has been studied, abstracted and correlated; and numerous tests have been made in the laboratory. The data indicate that dezincification may be successfully suppressed by about 0·03% of arsenic, antimony, or phosphorus without offsetting disadvantages. In a paper by C. S. Smith and R. W. van Wagner, a report on tension tests is given which were performed on copper and sixteen copper alloys in the form of commercially fabricated rods, using an extensometer sensitive to 0·0001%. Typical stress-strain curves are reproduced, together with curves showing offset and permanent set on a large scale, both before and after overstraining in tension. Overstrain decreases the stress—first producing measurable offset in annealed alloys, but increases the stress needed to produce an equivalent set. Heat-treated beryllium-copper follows Hooke's law to very high stresses if appropriate corrections for true stress and strain are made.

The results of short-specimen rotating-beam endurance tests are given by A. R. Anderson and C. S. Smith on commercially fabricated rods of tough pitch and oxygen-free copper and fifteen copper alloys, including precipitation hardening types. Endurance limits, at 300 million cycles,

are tabulated together with pertinent data on composition, fabrication and tensile properties, while the experimental data are presented in the form of S-N curves. The results are briefly discussed, and the fatigue machines, preparation of specimens, and testing technique are described.

Several papers presented were concerned with the finishing of die-castings. Aluminium die-castings, discussed by A. E. Keskulla and J. D. Edwards, are covered with a thin, transparent oxide film which constitutes one of their important advantages from a service point of view. For numerous applications, the ability of aluminium alloys to form and maintain this neutral film is sufficient protection, and further finishing is not necessary. For many other applications, however, where a more decorative appearance or better resistance to service conditions may be desirable, a wide assortment of durable and attractive finishes is available. These finishes, classed as mechanical finishes, chemical finishes, anodic finishes, electroplated finishes, paint and organic finishes, are discussed.

Magnesium die-castings, left to mild atmospheric weathering, as indicated by H. W. Schmidt, gradually acquire a layer of oxide, hydroxide or carbonate, which protects them from further attack. For most applications, however, the parts should be finished in some manner. The method adopted will depend on the requirements to be met. Diecastings used for interior applications such as business machines, household appliances, etc., are given finishes chosen for their decorative appeal and wearing qualities. For the various exterior applications protective finishing becomes more important and decorative considerations become secondary. All phases of metal finishing in use on magnesium die-castings are discussed, including preliminary mechanical finishing, cleaning, chemical treating and organic finishing.

In the use of any metal, E. A. Anderson states that consideration of the need for finishing is based on (1) the desire for decorative effects not obtainable in the metal itself; (2) the need for improved wear and abrasion resistance; and (3) the need for protection against special types of corrosive attack. Plated metallic, plated non-metallic, immersion non-metallic, and organic finishes may be used for decoration or for protection. In discussing the methods used with zinc alloy die-castings, each of the three main fields listed above is considered.

Effect of Temperature on Steel

A brief summary of the progress made during the year in the various research projects sponsored by the joint committee on effect of temperature on the properties of metals is one of the many committee reports presented. The projects include tests of tubular members at elevated temperatures, properties of metals at low temperatures, relation of torsion-creep and tension-creep, relaxation tests, and study of high-temperature test methods.

Among the papers presented was one on the effect of carbide spheroidisation upon the creep strength of carbon-molybdenum steel, by S. W. Weaver, in which the author states that the progressive changes in the properties of a steel with time at stress and temperature affect design stresses and the service life of high-temperature equipment. Test data were obtained from a plate of carbon-molybdenum steel cut into four parts and differently heat-treated to produce the following structures: fine grained normalised, fine grain annealed, coarse grained normalised, and coarse

grained annealed. In addition to the initial treatments, a part from each of the four groups was given a short and a longer spheroidisation time, making twelve different conditions of the material. Two independent long time-creep tests were run on each of the twelve conditions, one at 900° F. and one at 1,000° F., and the creep strengths so determined together with the resulting physical properties are reported.

Since considerable emphasis has been placed on the necessity for proper grain size, photomicrographs and macrographs are presented, in a paper by R. W. Emerson, to illustrate the effects of hot bending, upsetting, and welding on the microstructure of carbon-molybdenum steel in both the " as fabricated " and final heat-treated condition. In addition to microstructural analysis, results of hardness determinations, bend tests, and room temperature tension tests are given. A discussion of the effect of heat-treating temperature, cooling rate, and melting practice on the final grain size is given, including photomicrographs showing the coarsening characteristics of both coarse and fine grain (low- and high-coarsening temperatures, respectively) steel.

Several other papers were discussed at the same session. Thus, B. Johnston dealt with compression and tension tests of structural alloys. The tests include precise determinations of the upper and lower yield strength and modulus of elasticity, all in both compression and tension. All tests are made both with and across the direction of rolling. The materials include many of the currently used structural metals, such as carbon structural, silicon structural, six structural steels from various sources commonly called low-alloy, and copper-bearing nickel steels, together with several samples of structural aluminium alloy. There are over 35 different samplings of plate material, all from different heats. Included is a study of several variables involved in the testing technique.

The stress-strain characteristics of cold-rolled austenitic stainless steels in tension and compression are described by R. Franks and W. O. Binder. This paper also contains a procedure developed at the authors' laboratories for determining these properties of thin sheets of cold-rolled 18-8 steels in compression. This procedure will be of interest because the compressive properties of thin sheets are not easily determined, particularly when the material has such high strength.

Another interesting paper is that by H. Pray, R. S. Peoples, and F. W. Fink on a new free-machining addition for stainless steels. The authors state that the addition of small amounts of bismuth (0·1 to 0·5%) to the corrosion-resistant stainless alloys results in a remarkable and useful increase in their machinability with no detriment to, and in some cases, an improvement in their corrosion resistance. The paper describes laboratory data relative to the effect of bismuth on the machinability, corrosion resistance to a variety of media and conditions, physical properties at ordinary and high temperatures, galling resistance and the hot- and cold-working properties of several of the more common stainless alloy types. The general metallurgy of the bismuth-containing alloys is discussed. The laboratory data and results are substantiated by plant and service experience.

Fatigue of Metals, Corrosion of Iron and Steel

At this session the report of the research committee on fatigue of metals presented a detailed description of and results obtained in the investigation of the effect of different types of testing machines on the endurance limit of metals and on the shape of the S-N (stress-cycle) diagram. The machines studied included the rotating beam, the rotating cantilever beam, vibratory flexural, and direct axial stress. The tests were made on high-strength heat-treated alloy steel, medium-strength low-carbon steel, and an aluminium alloy (Duralumin). The report presents profilograph records, magnaflux tests, and photomicrographs of the metals studies, together with a series of curves and a discussion of the variation of endurance limits obtained

on the different machines; also the effect of shape of specimen and the endurance above the endurance limit.

In order to prevent the formation of fatigue cracks and the eventual breakdown of structural parts under the action of repeated stressing means have been employed for producing better surface finish and for artificially raising the endurance limit. W. M. Murray and J. M. Lessells present an analysis of the effects due to shot-blasting and its influence upon steels in different conditions. In some cases shot blasting can be very advantageous, but this depends upon the use to which the material is to be subjected as well as its condition. Test results are given to confirm the analysis and to illustrate the relative advantages due to this type of surface finish.

O. J. Horger and T. V. Buckwalter compare the fatigue of 7 in. diameter solid and tubular axles. Rotating cantilever beam fatigue tests were made on axles using steels having an analysis approximating S.A.E. 1045. Comparison of axle fatigue resistance due to a press-fitted wheel is made between " as forged " solid members and seamless tubes in " hot rolled " and several conditions of heat-treatment. Results show that tubular axles having high tensile strength values may or may not exhibit greater fatigue strength than those having lower physical properties. Observations on the effect of residual stresses are given. Some tubular axles show greater fatigue strength than the solid ones.

The form, size, and distribution of corrosion pits have been studied by D. J. McAdam, Jr., and G. W. Geil, after stressless corrosion of various steels in streams of well water, distilled water, and Severn River water, and in sprays of soft water and normal salt solutions. The results of the examination are correlated with the lowering of the fatigue limit, and with the effective stress-concentration factor. The effective stress-concentration factor depends on the form, size, and distribution of the pits and on the notch sensitivity of the steel. A discussion of the influence of cyclic stress (during corrosion) on the pitting of steels in well water and distilled water is presented.

W. P. Welch and W. A. Wilson describe a new machine for the rapid determination of the endurance limit of steels at high temperatures. The specimen is stressed in alternating bending at a frequency of 120 cycles per second, and is driven at constant amplitude by a reciprocating electro-magnetic motor supplied with 60-cycle power from the house line. Since the machine operates very close to resonance, an electronic control is provided to maintain constancy of amplitude despite the small changes in the line frequency ($\pm\frac{1}{3}\%$) which occur on a well-regulated power system. The results of operating experience over a period of one year is reported along with test results showing the quality of the data that have been obtained.

The effect of the amplification factor at or near resonance can be used advantageously in testing materials. The fundamental principle governing the investigations at or near resonance are discussed in a paper by R. K. Bernhard. An oscillator-driven endurance test machine based on the resonance principle is described more in detail, including control units and calibration. The main purpose of this machine is to test larger specimens and riveted or welded structural units; static and dynamic load conditions, alone or superimposed, can be produced at high frequencies, requiring a rather small power input for the driving motor. A few test data are presented.

As a part of an extended investigation of the atmospheric corrosion resistance of ordinary and low-alloy steels a test procedure and equipment have been developed which are capable of predicting in a few weeks the relative atmospheric corrosion rates for materials of this type. A paper by H. Pray and J. L. Gregg includes a general discussion of atmospheric corrosion testing, a description of the procedure and apparatus used for the accelerated test and a comparison of the accelerated and actual atmospheric tests for a number of commercial and special steels.

The Empire's Mineral Resources

Discoveries of new ore-bodies and developments in the mining industry in the past 25 years have contributed to the Empire's happy position.

EVERY material thing that man needs comes from the earth—everything that he eats, drinks, wears or uses, and all dwellings, transport facilities, tools, necessities or luxuries. Thus, agriculture and mining are regarded as the basic industries. But agriculture depends in part on mining, and, as many industries have been built and depend upon mineral raw materials, it can be said, therefore, that minerals hold a dominant place in modern life. Minerals are important in normal times and concern not only mineral industries but are important factors in national and international politics; in times of war, however, they become tremendously important from a strategic point of view. One instance of this is the mineral manganese, which is discussed elsewhere in this issue; over 90% of the consumption of this metal enters into steel manufacture for which it can be regarded as indispensable.

In peace-time the world's resources of minerals are available to all nations on the open market at world prices. In war-time, however, supplies of a particular mineral may be difficult to obtain or may entirely cease to be obtainable through the customary channels. Much has been written about the part played by minerals in war-time. We know that modern warfare, whether in the air, on the sea, or on land, necessitates the use of metals and minerals in far greater quantities than ever before. Some general aspects concerned with the production of mineral and metals, more especially in relation to the resources of the British Empire, were discussed by Mr. E. H. Clifford in his recent Presidential Address to the Institution of Mining and Metallurgy, in which he stated that the present consumption of the British Empire is much greater than the highest figure recorded in peace-time, yet, with few exceptions which are not serious in relation to the whole, sufficient supplies have been forthcoming. With the outstanding exception of oil, nearly all these supplies are produced within the Empire; this has been made possible by recent growth of the mineral industry without which supplies would have been severely limited.

During the period 1913-1938, world production of every mineral, except iron ore, increased. The greater increases were in what can be regarded as the "newer minerals," oil, aluminium, nickel, cobalt, tungsten, magnesium chromite and asbestos; whereas coal, copper, lead, zinc and tin showed smaller increases. The relative position of the Empire, on the whole, improved, remarkably in some cases during this period, and, with the exception of oil, is extremely well placed in respect of nearly every mineral. Among the more important of those derived from foreign sources are sulphur, potash and mercury, but on the other hand the Empire has large surpluses of several minerals available for export. All the large units of the British Commonwealth have abundant coal resources, and in Canada, South Africa, Australia and India the basis of industrial power has been laid by the building up of steel industries which are ample for their own requirements. Indeed, three of them are considerable exporters. In the mineral world the Empire's most important deficiency is oil; production is only $2\frac{1}{2}\%$ of the world's output and about one-fifth of her consumption. The commercial value of the production of coal, iron and oil far exceeds that of all other metals and minerals combined, but the latter are no less essential to modern industry, particularly in war-time, and it is to those that Mr. Clifford directed special attention.

Mention is made of the great increase in productive capacity of the base metals during the period under review. To say that this was due to normal development would be altogether too simple. No doubt the intrinsic mineral wealth of the Empire had a lot to do with it, but this can only be a partial explanation; there are several causes and to trace its beginnings it is necessary to go back to the early nineteen-twenties. This was a period of optimism in the economic world, culminating in the boom of 1929. It was a period of good metal prices and growing consumption which had a direct effect on the mining business. It was quite generally held that the consumption of metals had permanently resumed the same rates of annual increase which had prevailed for 50 years before the last world war and large construction programmes were laid down in this belief. At the same time there were significant technical advances in milling practice, in metallurgy, in economic geology, and, above all, in flotation. Without the revolutionary change brought about by flotation, for instance, there would have been little or no copper from Northern Rhodesia, or lead or zinc from the Sullivan Mine.

The mining laws of the British Empire, taken as a whole, can be described as good laws. Though differing in many respects, most of them provide that the disposal of the right to mine is in the hands of the State and not the owner of the surface. In most of the Dominions and Colonies free prospecting and a simple procedure to get secure title and the requisite surface rights are the general rule. In addition, the period was one of low income tax, judged by present-day standards, a vital consideration to mining enterprise registered in the United Kingdom.

These basic causes led to great general activity in the mining world from about 1912 until the end of the decade. In the early years there was widespread prospecting throughout the Empire. In Northern Rhodesia, for example, it led, in 1925, to the discovery of the copper ore-bodies which have greatly increased the production of Empire copper. At about the same time there were important discoveries and developments of gold, diamonds and manganese in West Africa, of asbestos, chromite and manganese in Southern Africa, and of tungsten in Burma. In Canada there was intense activity during the whole period, and the difficult metallurgical problem presented by the lead-zinc ore of the Sullivan Mine was overcome about 1920, and led, step by step, to the great production of to-day. Also in Canada, the Noranda Mine, discovered in 1912, was opened up in 1922, and at the same time the extraordinary value in nickel and copper of the Frood ore-body was disclosed by drilling. Both are now among the great mines of the world. In the lead-zinc-silver district of Broken Hill, New South Wales, extensive schemes of re-organisation and enlargement were undertaken at a later date and have recently been completed.

It is noteworthy to mention the Empire's dependence on a few districts. Great ore-bodies lend themselves to exploitation on a grand scale and considerably more than half of the Empire's output and about 30% of the world's output of gold, copper, lead, zinc and nickel are produced from only five districts, viz., the Rand, Sudbury, Northern Rhodesia, Broken Hill and the Sullivan Mine.

The hopes which gave rise to this activity were destroyed by the great economic depression which commenced in 1930. The base metal industry had to face much reduced consumption, over-equipment and low prices. Though the technical achievements were many and important, financial results were not commensurate with the outlay, and at the present time with a very large part of the production of base metals under contract to the Ministry of Supply at fixed prices, the position is not greatly improved to-day, though the enterprise shown has turned out to be of immense value to the nation. Had the developments been delayed a few years, the mineral production of the Empire would have presented a very different picture and there would have been grave deficiencies in our vital war requirements.

At the outbreak of the present war the Empire was much more favourably situated both in production of essential ores and smelter capacity than during the 1914-1918 conflict for which discoveries and developments of the mining industry were large responsible ; in addition, the advances of mining, concentration and smelting methods and extension of the use of hydro-electric power in some countries of the Empire have resulted in cheapening the cost of producton in comparison with those prevailing in 1914-18. Thus, for instance, electrolytic copper produced in Canada is being sold to the British Government at rather over 10 cents. per lb. as compared with about 26 cents. in 1914-15. Similarly, lead is being sold at rather over 3 cents. per lb. as against 8·5 cents. and zinc at 3·1 cents. as against about 8 cents. Canada's agreement to sell to the British Government the greater part of her production of these three metals at prices about those ruling just prior to the outbreak of war, represents a sacrifice of possible profits amounting to many million dollars ; a valuable contribution to the Empire's cause.

New Flake Pigments for Protective Paints

For several years past it has been appreciated that the advantageous properties of aluminium paints, particularly in respect of durability, protection of underlying metal against corrosion and reflection of light and heat, are due largely to the flake-like form of the pigment particles and their ability to leaf in the vehicle employed. This has lead to experiments, mostly unsuccessful, on the production of other pigments with this desirable combination of properties.

It is now claimed* that practically any pigment can be manufactured in the form of flakes by a recently patented process. In addition to controlling the shape of the pigment particles, this patent also claims that leafing properties may be conferred on the pigment flakes at will by a suitable modification of their surface. The possession of leafing properties causes the pigment flakes to tend to float to the surface and there to arrange themselves in planes parallel to the surface of the paint film.

This combination of properties has great beneficial effects on the paint film, improving especially its resistance to the penetration of moisture and corrosive influences. In view of the obvious advantages associated with a leaf or flake-like form of pigment particles in paint films. the value of a process which enables ar y pigment to be obtained in this form cannot be underrated. Paints made up with these new pigments will undoubtedly constitute a most welcome and possibly superior alternative to aluminium paints, especially at the present time when the use of aluminium is greatly restricted under Government regulations.

* British Patent Application No. 6444 (1941).

The Constitution and Properties of Cyanide Plating Baths

A REVIEW is given by Thompson* of some of the properties of the cyanide plating baths of the heavy metals based upon the probable constitution of the complex metallo-cyanides which are in solution. The purpose of the author is to summarise the available information on the constitution of the complexes in cyanide plating baths and to aid in planning further researches. Emphasis is laid upon the fact that the cyanide complexes form a general group of co-ordination compounds.

In the discussion of individual metals an attempt is made to correlate qualitatively some of the properties of cyanide plating baths, particularly current efficiency and polarisation, with their probable constitution. The agreement between different investigators is not always close, largely because of the lack of standardisation of apparatus and methods and the difficulties of measurement with these unstable solutions.

For convenience, a summary of the probable constitution of the common cyanide plating baths is given in the accompanying table. No claim can be made for exactness, and the table may need revision from time to time. In the control of plating baths it is customary to employ

PROBABLE COMPLEX IONS PRESENT IN CYANIDE PLATING BATHS AT ROOM TEMPERATURE.

Bath	Major Complex Ions	Minor Complex Ions
Copper	$Cu(CN)_3^{--}$	$Cu(CN)_2^-$, $Cu(CN)_4^{---}$
Silver	$Ag(CN)_2^-$	
Gold	$Au(CN)_2^-$	
Zinc	$Zn(CN)_4^{--}$, ZnO_2^{--}	$Zn(CN)_3^-$
Cadmium	$Cd(CN)_4^{--}$	$Cd(CN)_3^-$,† $Cd(CN)_2$
Brass	$Cu(CN)_4^{---}$, $Zn(CN)_4^{--}$	$Cu(CN)_2^-$, $Cu(CN)_3^{--}$, $Zn(CN)_3^-$

some quick, simple titration for determining the content of excess cyanide, or free cyanide. Such a method is an indirect and sometimes arbitrary means of determining the complex present. This procedure is quite accurate for silver and probably for gold, but is only approximate for copper, cadmium and brass. With zinc baths it has been found most satisfactory to determine the total cyanide and total alkali, without attempting to assign the distribution of zinc between them. Except for silver and gold baths, there is much to be said at the present time for the determination of total cyanide by the distillation method and for control by the principle of the cyanide ratio rather than by the free cyanide content. This may be especially useful for brass baths. However empirical this may seem, it has the advantage of eliminating numerous uncertainties and of placing all the baths upon the same basis. Perhaps we are accustomed to exaggerate the importance for control (not for research) of the free cyanide concentration. We do not ordinarily correlate this value with the probable composition of the electrode films, the operating bath temperature, or even the actual metal being deposited. For example, a standard silver solution is employed for analysing baths of other metals.

Progress in understanding the relation between structure and properties of the complex cyanides appears to depend largely upon the systematic application of the Werner co-ordination theory.

It is evident that the subject of deposition from the cyanide baths still includes a number of unsolved problems, particularly for such metals as copper, silver, thallium, zinc, cadmium, lead and indium.

Metal Barrels and Tin Plate Goods

UNDER a Board of Trade Order which came into force on 19th June, 1941, licences will be required to export to all destinations metal barrels and drums and certain articles manufactured wholly or mainly from tin plate or terne plate.

* M. R. Thompson, Electrochemical Society, General Meeting, 1941, Preprint 79-7.
† Cadmium cyanide, which may be slightly ionised.

The Effect of Antimony on Magnesium

By Professor W. R. D. Jones, D.Sc., and L. Powell, B.Sc.

Experiments have been conducted to determine whether antimony forms a solid solution with magnesium and the effect of antimony on the mechanical properties of magnesium. It is shown that antimony does not cause any improvement of the mechanical properties or corrosion-resisting properties. The solid solubility of antimony in magnesium is very small and the alloys are not capable of age-hardening.

Abridged.

IT is now more or less established that the only metals which may be added to increase the mechanical properties of magnesium are those that form solid solutions. Hume-Rothery has shown that solid solutions cannot be formed to any extent if the difference between the atomic diameter of magnesium and that of the added metal is more than about 14%. One of the metals coming within this limit is antimony, some of the characteristics of which show a certain similarity with those of magnesium. Unfortunately antimony forms a compound with magnesium which has an embrittling effect. No evidence, however, has been published that antimony does not form a solid solution with magnesium, and if antimony does go into solid solution, even to a very limited extent, useful alloys may be obtained.

In recent years attention has been directed to the antimony-magnesium alloys by other workers, who indicated that small percentages of antimony seemed to be of some benefit to magnesium, and the experiments described in the present paper[*] have been carried out to determine (a) whether antimony forms a solid solution with magnesium, and (b) the effect of antimony on the mechanical properties.

The liquidus and solidus temperatures of a number of alloys[†] with a relatively low antimony content were determined in a manner similar to that described previously.[1] The antimony in the alloy was determined either by the usual potassium bromate method, or, if low, by the Reinsch method.[2] The arrest points on the cooling curves are given in Table I. The antimony content of some of the alloys was so low that the arrest point was not very definite. Accordingly the temperatures of the beginning and the end of the arrest are given as well as that of the maximum time halt.

TABLE I.
THE ARREST POINTS ON THE COOLING CURVES.

Antimony, %	Primary Arrest Temperature, °C.			Eutectic Arrest Temperature, °C.		
	Start	Maximum	End	Start	Maximum	End
nil	650·5	648	646	—	—	—
0·11 R	651	649	647	630·5	630	629
0·15 R	650·5	649	647	—	—	—
0·28 R	652	641	648·5	630·5	indefinite	indefinite
0·30 R	652	651	648·5	631+	631	630
0·48	651	649·5	648	631	628·5	627·5
0·50	651	650	648·5	631	630·5	629·5
0·62	653	650·5	647	631	631—	—
0·73	649·5	649	647	631	630·5	629
0·75	653·5	650	648	631	629·5	628·5
0·77	650	649	648	630·5	629	628·5
1·15	652	650	647	630·5	629·5	625
1·24	649·5	548·5	647	630	629	628·5
2·03	648·5	648	646·5	630·5	629·5	628·5
4·20	644	643	641	631	628·5	627·5
5·02	645·5	641	639·5	631	629·5	628·5

In alloys marked R the antimony was determined by the Reinsch method.

* *Jour. Inst. Metals*, 1941, **67**, pp. 177-188.
  † Pure redistilled magnesium guaranteed to be 99·99% magnesium, and commercially pure antimony with arsenic guaranteed no more than 0·02%, were used in making the alloys.
1 W. R. D. Jones, *J. Inst. Metals*, 1931, **46**, 395.
2 S. G. Clarke and B. S. Evans, *Analyst*, 1929, **54**, 23.

On examination under the microscope each alloy, after polish attack with "Silvo" and 2% alcoholic nitric acid, showed that the compound Mg_3Sb_2 was present in the form of pale dove-grey particles.

Certain of the ingots which had been used for the determination of the critical points were cast into bars $1\frac{1}{8}$ in. in diameter and forged to rods of $\frac{1}{2}$ in. diameter. Small specimens from these rods were given an annealing treatment for one week at temperatures controlled to ± 1° C. They were packed into partly evacuated Pyrex tubes into which were also sealed the two wires of a platinum/platinum-rhodium thermocouple. At the end of the annealing period the Pyrex tubes were immersed in cold water and quenching of the specimens was practically instantaneous. The rods were usually homogeneous, but in cases of doubt the whole specimen was used in the chemical analysis after the heat-treatment and microscopical examination. The alloys used had the following percentage compositions : 0·10 (R).[†] 0·17 (R), 0·26 (R) 0·34 (R), 0·41, 0·46, 0·76, 0·95, 0·96, 1·19 and 2·16., The annealing treatments were carried out at 300°, 350°, 400°, 450°, 500° and 550° C. At higher temperatures the couple wires were attacked by magnesium and/or antimony vapour. In the forged condition the alloys showed some evidence of micro-shrinkage. The compound occurred as isolated laths, generally in the grain boundaries forming a more or less discontinuous envelope, depending on the antimony content. A eutectic structure was formed when the antimony exceeded more than about 1%. After annealing the compound was not connected with the grain boundaries and was globularised. Particles of compound were present in all the alloys after annealing at each temperature up to 500° C. ; after annealing at 550° C. for one week there was no trace of compound in the alloys containing 0·104 and 0·17% antimony, but it was definitely present in the alloy containing 0·26%. Therefore it can be stated that from the results of these experiments the solid solubility of antimony in magnesium is less than 0·1% at temperatures up to 500° C. and less than 0·2% at 550° C.

Various ageing experiments were carried out on sections of 1 in. diameter bars by giving them a solution heat-treatment at temperatures up to 550° C. for 24 hours followed by quenching in water. The same specimens were tempered at 160° C. for eight hours and cooled in air. Hardness tests were made before and after treatment on a Firth Variable-Load Hardometer using a diamond indenter and a load of 5 kg.[‡] sustained for 30 sec. The test results proved that the alloys are not susceptible to age-hardening and confirm those which showed that there is little solid solubility of antimony in magnesium.

† R means that in this alloy the antimony was determined by the Reinsch method.
  ‡ The use of a larger load with a diamond or ball indenter will give, in the case of magnesium and many of its alloys, a very imperfectly shaped impression which is difficult to measure and which may lead to inconclusive figures.

The Mechanical Properties of the Alloys

Chill-Cast Alloys. The magnesium used for melting was in the form of 1 in. diameter cast rods which had the following analysis : Silicon 0·026%, iron 0·046% and manganese 0·012% ; zinc, copper and lead nil ; remainder magnesium. The antimony was added in the form of a hardener alloy containing 20% antimony. The method adopted for melting and casting the alloys was, in general, that described previously.[3] The magnesium rods were melted in a bottom-pouring steel crucible which had a tightly fitting lid, carrying a stirrer and a steel thermo-couple sheath. "Elrasal" flux previously fused and in amount equal to about 2½% to 3% by weight of metal melted was used. During the whole of the melting operation the bath was controlled as to time and temperature. The metal was teemed into a group-casting iron mould the temperature of which was about 450° C. By this means a group of five ingots of 1 in. diameter and 8 in. length was obtained, each ingot of which should have been identical with all the others. Two heat-treatment procedures were adopted : (1) the cast bars were placed in an electric muffle furnace automatically controlled at 450° C. and maintained at this temperature for one hour, after which they were withdrawn and cooled in air ; (2) the cast bars were placed in the electric furnace automatically controlled at 350° C. and maintained at this temperature for eight hours, and then the current was switched off and the bars allowed to cool down with the furnace to the ordinary temperature. The tests were not carried out until at least four days had elapsed after the machining of the specimens. The results of the tests are given in Tables II., III. and IV.

TABLE II.
THE TENSILE PROPERTIES OF 1 IN. DIAMETER CAST BARS.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	1·2	6·9	7	6½
trace	1·2	6·8	—	—
0·32	1·3	6·3	6	5½
0·34	1·3	6·3	6	5½
0·45	1·4	6·2	6	5½
0·59	1·5	6·2	5½	5
0·66	1·5	6·2	5½	5
0·84	1·6	6·0	5	5
1·04	1·7	5·8	5	4½
1·74	1·8	5·4	4½	4
2·14	1·8	5·3	4	3½
2·58	1·9	5·2	4	3
3·38	2·0	5·0	4	3
3·98	2·2	5·0	4	3
4·09	2·3	4·9	4	3
4·32	2·3	4·8	4	3
4·95	2·6	4·7	3	3

TABLE III.
THE TENSILE PROPERTIES OF 1 IN. DIAMETER CAST BARS AFTER ANNEALING AT 450° C. FOR 1 HOUR.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	1·53	6·4	7	6
trace	1·5	6·0	6	6
0·32	1·5	5·7	5½	5
0·34	1·4	5·7	5	5
0·45	1·5	6·1	5	5
0·59	—	6·0	4½	4½
0·66	1·5	6·0	4	4½
·84	1·6	5·9	4	4½
1·04	1·6	5·8	4	4½
1·74	1·8	5·6	3½	4
2·14	1·8	5·5	3½	4
2·58	1·8	5·3	3½	4
3·38	2·0	5·0	3	4
3·98	2·0	4·9	3	4
4·09	2·0	4·9	3	4½
4·32	2·1	4·8	3	3½
4·95	2·4	4·7	3	3½

Summarising these results it can be stated that there is no advantage in adding antimony to magnesium for casting alloys—the only property which was improved was the proof stress, and this improvement is probably not commensurate with the increase in density caused by the addition of antimony. Several other metals when added to magnesium will give casting alloys with much better mechanical properties.

3 W. R. D. Jones and K. J. B. Wolfe, *J. Inst. Metals*, 1938, **62**, 156.

The hardness values were determined with a Firth Variable-Load Hardometer using a diamond indenter and a load of 5 kg. imposed for 30 sec. The values were determined on cross-sections and on longitudinal sections prepared near the outer surface of the bars. The values are given in Table V. Each value is the mean of five fairly concordant results. The effect of antimony on the hardness in all the conditions treated was slight.

Rolled Alloys.—Ingots for rolling were produced by the same method as that used for chill-cast bars. The alloy was teemed into a vertical cast-iron mould of 1½ in. internal diameter, having a runner of ¾ in. diameter along the whole length of the ingot mould and connected to it by a narrow gate which also ran the whole length of the mould. This enabled an ingot with a good surface to be produced with little if any depression on the top due to piping, because all contraction was confined to the runner. The ingots did not require machining before rolling, which was carried out in a 3-high, 24 in., non-reversing mill using a rolling speed of 60 ft. per minute. The rolls were pre-heated to about 80° to 90° C. The ingots were heated for 1 hour at 450° C. and then rolled to ⅞ in. diameter, care being taken not to force the reduction ; the bars were given frequent intermediate reheatings at 450° C.

The mechanical properties were determined in the "as-rolled" condition, after annealing at 450° C. for 1 hour and cooling in air, and after annealing at 350° C. for 8 hours and cooling slowly in the furnace.

Table VI. gives the mechanical properties of the bars as rolled, from which it can be seen that the addition of about ½% of antimony increased slightly the proof stress and ultimate stress, but decreased the elongation and reduction of area figures. The addition of further antimony decreased

TABLE IV.
THE TENSILE PROPERTIES OF 1 IN. DIAMETER CAST BARS AFTER ANNEALING AT 350° C. FOR 8 HOURS.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	1·3	6·1	5	4½
trace	1·3	6·0	5	4½
0·32	1·3	6·3	4½	2½
0·45	1·4	6·5	4½	2½
0·66	1·5	6·5	4	2
1·74	1·7	6·4	3½	2
2·58	1·6	5·8	3	2
3·98	2·0	5·6	2½	2
4·09	2·0	5·4	2½	2

TABLE V.
THE HARDNESS OF THE CAST ALLOYS.

Antimony, %	As Cast			Cast and Annealed 1 hour at 450° C.			Cast and Annealed 8 hours at 350° C.		
	Cross-Section	Longitudinal Section	Difference	Cross-Section	Longitudinal Section	Difference	Cross-Section	Longitudinal Section	Difference
nil	30	43	13	32	36	4	36	40	4
trace	30	46	16	33	39	6	35	41	6
0·32	31	47	16	31	40	9	36	41	5
0·45	31	47	16	32	39	7	36	42	6
0·66	32	46	14	32	41	9	35	39	4
1·74	33	44	11	33	40	7	37	43	6
2·58	34	49	15	33	39	6	36	40	5
3·98	33	48	15	34	42	8	38	43	5
4·09	33	48	15	34	42	8	38	43	5

TABLE VI.
THE TENSILE PROPERTIES OF ROLLED BARS.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	6·9	12·3	5½	6½
0·16	7·4	12·4	3	3
0·65	7·5	12·5	2½	2½
2·07	7·6	12·0	1	1½
3·39	8·0	14·1	1	2

ductility but without impairing the tensile properties. The mechanical properties of the low-antimony alloys were not improved by annealing at 450° C. for 1 hour (Table VII).

Similar results were obtained after annealing at 350° C. for 8 hours (Table VIII).

The effect on the fractures of the tensile test-pieces of the addition of antimony to magnesium was to decrease the coarseness and with more than about ½% addition the fractures became "dry," losing all silkiness, and were

similar to those of cast-iron ; they were readily tarnished on exposure to the atmosphere. The fractures of bars with the same antimony content were not affected much by heat-treatment.

The hardness values are given in Table IX.

Corrosion Tests

The corrosion-resistance of the alloys was tested by a three weeks' salt-water-mist test. Discs $\frac{1}{8}$ in. thick were prepared from rods of 0·8 in. diameter. The surface of the specimens was as " fine machined " and substantially smooth. For the purpose of degreasing before exposure they were rubbed lightly with magnesium oxide on wet cotton wool, then washed in water, dipped in acetone, and finally dried. Weighed specimens of about 0·8 in.² area were exposed horizontally in a cabinet for three weeks to an intermittent salt-water-mist consisting of natural sea water taken from the English Channel (near Rye). A dense mist was produced for 20 minutes twice a day, and

TABLE VII.
THE TENSILE PROPERTIES OF ROLLED BARS AFTER ANNEALING AT 450° C. FOR 1 HOUR.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	6·7	11·5	3½	4½
0·16	6·8	11·6	3	3½
0·65	7·9	12·1	2	3
2·07	7·9	11·7	1½	2½
3·39	7·7	11·5	1	1½

TABLE VIII.
THE TENSILE PROPERTIES OF ROLLED BARS AFTER ANNEALING AT 350° C. FOR 8 HOURS.

Antimony, %	0·1% Proof Stress, tons/in.²	Ultimate Stress, tons/in.²	Elongation % on 2 in.	Reduction of Area, %
nil	4·2	11·4	3½	4½
0·16	7·6	11·5	2½	2
0·65	7·3	12·3	3	3
2·07	8·6	13·0	2	2½
3·39	7·9	13·4	1½	2½

TABLE IX.
THE HARDNESS OF THE ROLLED BARS.

Anti-mony, %	As Rolled			Rolled and Annealed at 450° C.			Rolled and Annealed at 350° C.		
	Cross-Section	Longi-tudinal Section	Differ-ence	Cross-Section	Longi-tudinal Section	Differ-ence	Cross-Section	Longi-tudinal Section	Differ-ence
nil	30	30	0	31	30	1	30	30	0
0·16	30	31	−1	32	32	0	33	31	2
0·65	34	32	2	32	30	2	32	32	0
2·07	33	34	−1	33	34	−1	36	33	3
3·39	37	36	1	38	34	4	36	35	1

TABLE X.
CORROSION TESTS.

Antimony, %	Weight of Metal Corroded, grm.		Remarks
	Forged	Cast	
nil	—	0·055	Uniform corrosion.
nil	0·057	—	" "
nil	—	0·055	Rather large grains in relief.
nil	—	0·067	" " " "
trace	—	0·048	" " " "
trace	—	0·053	" " " " slight pitting.
trace	0·045	—	Uniform corrosion.
trace	—	0·054	Rather large grains revealed in relief.
0·16	—	0·073	Surface roughened, slight pitting.
0·16	0·012	—	Slight localised corrosion in concentric rings.
0·65	0·019	—	Slight localised corrosion.
2·10	—	0·103	Deep pitting.
2·10	0·055	—	Surface roughened.
3·40	—	0·116	Deep pitting.
3·40	0·168	—	Surface roughened.
AM 503 (2% manganese)		0·008	Very slight corrosion.
AZ 91 (to specification D.T.D. 281, solution-treated)		0·008 0·008	" " "

slowly dispersed by slight ventilation in the cabinet. At the end of the trial any salt incrustation was washed off in water. The corrosion product was removed by boiling for two minutes in 10% pure chromic acid without attacking the basis metal. The loss in weight was determined and the specimen was examined superficially. The results of the tests are given in Table X.

From the results obtained it can be said that small amounts of antimony appeared to improve the corrosion-resistance of the forged material, but produced the opposite

effect with cast material. Larger amounts (over 2%) reduced the corrosion-resistance of the material in either condition. The Elektron alloys AM 503 and AZ 91 were much more resistant to corrosion than any of the forged or cast antimony-magnesium alloys.

Conclusions

The main conclusions which can be drawn from this work are :—

1. The alloys are readily melted and can be easily cast.
2. The solid solubility of antimony in magnesium is very small, being less than 0·1% at temperatures up to 500° C. and less than 0·2% at 556° C.
3. The alloys are not capable of age-hardening.
4. The addition of antimony to magnesium causes no increase in tenacity or ductility either in the cast condition or after heat-treatment, but there is an improvement in the proof stress. The rate of decrease in the mechanical properties of cast bars with increasing antimony content reaches a maximum with ½% to 1%, after which the decrease is not as serious. The mechanical properties are improved by annealing at 450° C.
5. Ingots containing up to 4% antimony can be readily hot rolled, yielding bars with a higher tenacity and proof stress than rolled magnesium. Prolonged annealing at 350° C. gives improved tensile properties. The ductility figures are, however, low before and after annealing.
6. Pure magnesium is known to be weak mechanically, and the addition of antimony makes it, in general, appreciably weaker.
7. The addition of antimony to magnesium does not confer any notable corrosion-resisting properties.

Mould and Core Treatment in Die-casting

PRESSURE and gravity die-casting is to-day a repetitive process in which added care must be given to the treatment of moulds and cores. In recent years, improved methods have enabled castings to be turned out without machining or buffing to produce a suitable external finish. Much thought has been given to the subject of parting and, coupled with the better knowledge about alloy compositions, temperatures and pressures, has brought about an all-round saving in production time and costs.

The first quality required in a parting medium is resistance to temperature and absence of any tendency to gas. Owing to the fact that it forms a slippery inert and temperature-resisting graphite film on dies, moulds and cores, " Aquadag " colloidal graphite in water is now standardised by large die-casters. As some doubt exists as to the best method of treatment, it should be stated that all faces to be coated should first of all be degreased with white spirit, petrol or other suitable solvent. The " Aquadag " is then diluted with approximately ten parts by weight of distilled water and the resulting solution sprayed or brushed on to the cleaned mould surfaces. If this is carried out after a casting operation the residual heat in the moulds and cores will dry off moisture and leave a dry graphite film. When the latter is first being put into service, two or three applications may be made in succession and the resulting coating lightly polished with a dry, clean rag.

Thereafter, the frequency with which the moulds will have to be treated would depend on the through-put of castings, but in some cases it will be found to last a considerable time and require only occasional light renewal by a quick brushing of the solution.

Where chilling of the cores between casts is adopted, a dilute solution made up of one part of " Aquadag " in one hundred parts of water can be used as a core wash, being brushed on to the surfaces of the latter. A dispersion of colloidal graphite in oil is recommended by certain manufacturers of die-casting equipment for the lubrication of external moving parts on machines. In this connection, it should be remembered also that the graphite film so formed is an excellent high temperature lubricant, and is used for that purpose on furnace bogies, kiln car axle bearings and in other work where heat is a problem.

Service Experience with the Newer Condenser Tube Alloys

Where service conditions are severe, adoption of the newer alloys is taking place quite generally.

IN recent years a number of alloys have been developed for condenser tubes which offer greater resistance to fouling under certain conditions than the older alloys used for this purpose, and a report* dealing with service experience with these newer alloys is of considerable interest. The material for this report was obtained in response to an inquiry sent to 162 organisations representing the largest operators of land and marine surface condensers and several condenser tube manufacturers. It covers experiences with the newer condenser tube alloys, such as aluminium brass, aluminium bronze, copper-nickel, copper-nickel-tin, and copper-nickel-zinc, of which a large tonnage has been installed in the past 10 years.

The stations on uncontaminated inland rivers and lakes reported continued success with the older alloys of Admiralty, Muntz and arsenical copper alloys. The adoption of the more expensive alloys probably cannot be justified in stations where the older alloys are giving from 70,000 to 120,000 service hours with few failures. Where service is severe, however, adoption of the newer alloys is taking place quite generally. Firms using salt or brackish circulating water in their condensers were all in favour of the newer condenser tube alloys. The newer aluminium or nickel-bearing alloys resist dezincification, and are more effective in eliminating failures from this source. The aluminium-bearing alloys resist impingement attack better than the older type alloys.

In many stations where the older alloys have not given satisfactory service, trial installations were made to select the alloy best suited to the particular conditions. The trial installations usually consisted of batches of the newer alloy tubes installed in one or more of the condensers.

A company operating condensers with harbour circulating water carrying coke and ash particles that lodged in the tubes, and excessive amounts of entrained air that caused severe inlet end impingement attack, found that alloys containing aluminium have a much longer life than nickel alloy or Admiralty metal tubes. This is due to the fact that dezincification does not occur and that inlet end corrosion resulting from impingement attack is greatly decreased. Another seaboard company found that an experimental installation of aluminium brass tubes outlasted two sets of Admiralty tubes, and as a result equipped two condensers with aluminium brass tubes which to date have given very satisfactory service. Short-time tests, designed to permit a fairly quick determination of the relative values of the various alloys, have been undertaken by a number of companies.

One company made a test of 39 tubes representing 12 different alloys. Short lengths of the tubes were placed in a rack, which in turn was placed in the inlet water-box of one of the main unit condensers, about 8 in. in front of the tube sheet, so that the samples were directly in the flow of the circulating water and subjected to its full turbulence. Each sample was accurately weighed at the start of the test and also at 6-month intervals thereafter. This weight when compared with the original weight gave the percentage loss in weight for the sample.

A wide variation in the performance of the tubes was noted. A study of the data indicated a distinct grouping of the tubes according to their chemical compositions. The first group (lowest percentage loss in weight) includes only those tubes containing aluminium ; the second group the cupro-nickel tubes ; and the third the Admiralty and miscellaneous alloys. The divisions between the groups are marked, and indicate that this grouping is no accidental occurrence.

A study of the aluminium brass samples indicated that the annealed tubes are superior to the hard-drawn tubes and, further, that the optimum aluminium content is close to 2·5%. The conclusions are based on the tests reported above and not on service experience.

Stations operating under conditions peculiar to their particular locations have experimented to determine the alloy best suited to their individual problems. An example of this is the investigation made by a public utility company with a station on an inland river contaminated with acid drainage water from nearby mines. This investigation led to the conclusion that at this station metals that resist salt water and alkaline water do not resist acid mine water. In a test under actual service conditions an alloy of 88% copper, 10% zinc, 2% tin showed up best of eight alloys tested—better than 70/30 copper-nickel ; Admiralty ; aluminium brass ; aluminium bronze ; arsenical copper ; 70% copper, 29% nickel, 1% tin ; and 70·5% copper, 26% zinc, 2% aluminium, 1·5% nickel.

A second test was made by suspending plates of 20 alloys and nickel in the water box of a condenser. It was established from this test that alloys containing a high percentage of chromium are the only ones that completely resist the acid-water corrosion. Alloys containing nickel were poor and pure nickel extremely poor.

The tests are being continued with condenser tubes of seven different alloys :—

18% chromium, 8% nickel, 74% iron (stainless steel).
18% chromium, 82% iron (stainless iron or chrome iron).
88% copper, 8% zinc, 4% tin.
99·92% copper, 0·025% phosphorus—plus some silver.
98·9% copper, 0·27% zinc, 0·45% chromium.
Red brass (85% copper, 15% zinc).
Phosphorised admiralty.

The Navy Department, Bureau of Ships, has, under actual service test aboard ship, condenser installations containing tubes made of the following different alloys apart from the standard installations of Admiralty and 70/30 copper-nickel alloy :—

|	
Copper-nickel-tin.	Nickel-copper (Monel).
Aluminium-copper-nickel.	Dorium " D " metal.
Copper-nickel-zinc.	Copper-nickel (hard drawn).

The Bureau of Ships continues to specify the use of 70/30 copper-nickel tubes and tube sheets in the construction of all heat exchangers, including condensers employing salt water as the cooling medium. From a comparison with other alloys under actual service conditions 70/30 copper-nickel tubing has demonstrated high corrosive-resistant qualities. With the zinc content of this alloy kept within the limit of one-half of 1%, the failure of condenser tubes from dezincification is practically eliminated. It has been definitely established that Admiralty metal tubes are capable of withstanding direct impingement action of either steam or salt water better than 70/30 copper-nickel tubes, although Admiralty tubes are subject to failure as the result of dezincification.

To date the performance of 70/30 copper-nickel tubes has been most satisfactory, and none of the above-mentioned alloys has proved superior to 70/30 copper-nickel. The condenser installations in which the above tubes are provided vary from 100 sq. ft. to 10,000 sq. ft. in condensing surface. The length of service during which the above-mentioned tubes have been under test varies from 12 months to 6 years. The area of greatest failures has been either at the top of the tube bank or in the path of the
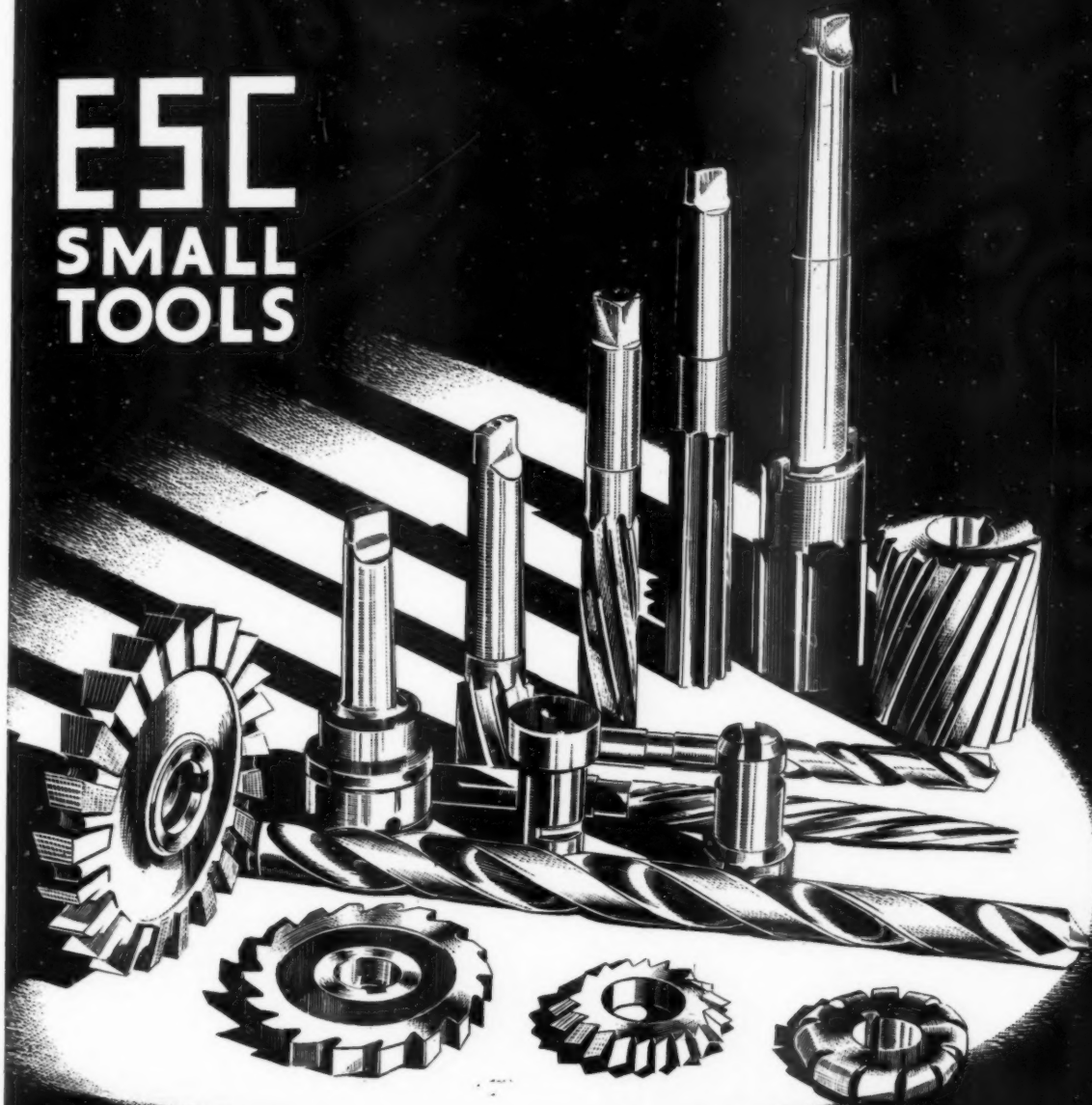
Intergranular Corrosion in Austenitic Stainless Steels

By J. H. G. Monypenny, F.Inst.P.

The occurence of intergranular corrosion in austenitic chromium-nickel steels, its detection, cause and prevention and the effects it produces, are discussed. In the practical application of these steels this trouble has been largely overcome, though not entirely, and in this article the author takes stock of the present position, studies in some detail the effect of different variables, and points out where satisfactory results can be obtained in the industrial use of the steels and where further improvements are still desirable. Attention is given mainly to the 18-8 steels, as these are the most widely used of the austenitic stainless steels, but the author emphasises that intergranular corrosion is not confined to steels of this composition.

THE effects of intergranular corrosion in austenitic chromium-nickel steels of the " 18-8 " type were probably first observed about the middle of 1926, when it was noted that equipment made in these steels occasionally cracked or became porous in service. Often there was little or no evidence of corrosive attack on the surface of the part affected ; the steel appeared suddenly to have cracked or become hopelessly brittle locally. Some difficulty was experienced at first in finding the cause of these failures—which occurred mainly in chemical plant—until it was realised that they were a product of two successive actions :

(a) Certain forms of heat-treatment followed by
(b) Corrosion.

Until the steel suffered corrosive attack its properties, after being wrongly heat-treated, were still good ; some slight loss in ductility and toughness might be observed, but it was quite insignificant compared with the embrittlement found in practice. On the other hand, when the wrongly treated steel was subjected to corrosive action—often of a character which normally would have no effect on the steel—it was prone to crack when lightly stressed, and in extreme cases would crumble to powder. Observation showed that

(a) Material which proved defective in this manner had been heated during fabrication processes to a dull red heat (roughly 500°-900° C.), or had been cooled otherwise than quickly from the normal heat treatment temperature (1,100° C. or so) used for softening worked material ;
(b) It differed structurally from the normal form in that the grains of austenite, of which the steel should consist entirely, were separated from each other by thin films of carbide ;
(c) Corrosion proceeded along these carbide-containing grain boundaries, and was frequently confined entirely to them.
(d) Material structurally liable to undergo this intergranular attack could be restored to its normal corrosion-resistant state by reheating to the correct softening temperature and then cooling rapidly ; this treatment also removed the carbide membranes.

It appeared reasonable to assume, therefore, that the peculiar intercrystalline attack was connected with the formation of carbide membranes separating the austenite grains.

So far as the author is aware the first published account of the production and prevention of intergranular corrosion was given by two of his colleagues—Messrs. H. Bull and L. Johnson—in a lecture to the British Acetylene and Welding Association in London, on March 29th, 1928, and was published in their journal *Industrial Gases* the same month.[1] A somewhat abridged form of the lecture, together with further information added during the

discussion, was issued about the end of 1928 by Brown, Bayley's Steel Works Ltd. in their journal.[2] Since that time a large number of papers and articles have appeared, in the transactions of various technical societies and the columns of the technical Press, dealing with the occurrence of intergranular corrosion, its detection, cause and prevention. The mass of data in these publications is not always in agreement, probably because some of the earlier papers were written at a time when knowledge of the cause of the trouble and the effects of different variables was less extensive than now ; the experimental conditions adopted were not always the most suitable for the purpose and the deductions from the results not always sound. In many respects the trouble has been successfully overcome in the practical application of the steels, though not in all cases. It may be useful to take stock of the present position, to study in some detail the effect of different variables, and to point out where satisfactory results can be obtained in the industrial use of the steels and where further improvements are still desirable. For convenience, attention will be given mainly to the class of steels frequently known as the " 18-8 " type—which may contain 15/20% chromium, 8/12% nickel and up to about 0·15% carbon—as these are the most widely used of the austenitic steels, but it should be pointed out that intergranular corrosion is not by any means confined to steels falling within this range of composition. It has been shown to occur in austenitic chromium-nickel steels whose composition varies between limits at least as wide as 10/25% chromium and 8/36% nickel, in similar steels to which certain other alloys have been added and in austenitic chromium-manganese steels.

It may be useful first to describe briefly the generally accepted theory of the cause of intergranular corrosion and the methods which have been used for detecting susceptibility, and afterwards to consider more fully various factors which are of particular importance in the industrial application of the steels.

As mentioned above, the primary cause of the production of intergranular corrosion appeared to be the precipitation of a network of carbide round the grains of the austenite, and early observation indicated that susceptibility increased broadly with carbon content. The formation of the carbide itself was shown by Bain and Aborn,[3] and by Houdremont and Schafmeister[4] to result from the low solubility of carbon in the chromium-nickel austenite at temperatures below about 900° C. The results obtained by Bain and Aborn and founded upon experiments very carefully conducted so as to obtain equilibrium, are given in curve A in Fig. 1. The data obtained by the German investigators indicated a rather more gradual change in solubility with temperature, their values being higher than

1 " Welding of Stainless Materials," H. Bull and L. Johnson, *Industrial Gases*, March, 1928, p. 8.

2 " The Welding of Stainless Steels," *Brown, Bayley's Journal*, No. 5.
3 " Nature of the Nickel-Chromium Rustless Steels," E. C. Bain and R. H. Aborn, *Trans. Am. Soc. Steel Treat.*, Vol. XVIII (1930), p. 837.
4 " Prevention of Intergranular Corrosion in Steels containing 18% Cr. and 8% Ni." E. Houdremont and P. Schafmeister, *Archiv. f.d. Eisenhüttenw.*, Vol. VII., p. 187 (Sept., 1933).

Bain's below 950° C. and lower at higher temperatures as shown in curve B, Fig. 1 ; as however they do not appear to give details regarding the methods they employed, critical comparison of their results with Bain's is difficult. It may be noted, however, that they suggest their values are only approximate.
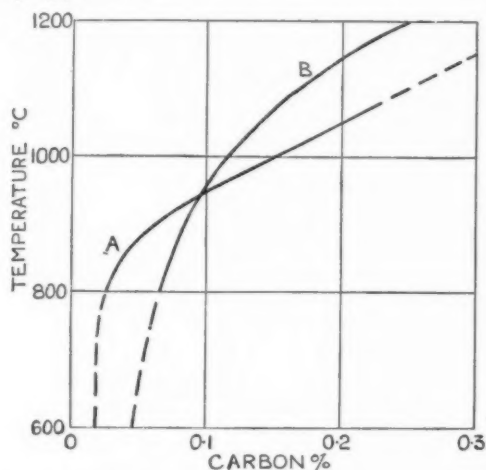

Fig. 1.—Solubility of carbon in " 18-8 " steels. Curve A : Bain and Aborn (3). Curve B : Houdremont and Schafmeister (4).

At first there was some uncertainty as to how the carbide membrane caused intergranular corrosion, thus Payson[5] considered that it was the "incipient precipitation of carbon rather than the definite formation of carbides " which caused attack ; he was apparently led to this idea because he could not detect carbides microscopically in steels heated for short periods at, e.g., 700° C., which, however, were definitely susceptible to intergranular attack. It seems probable that his microscopic examination was based on samples etched with Murakami's re-agent, and the difficulty in detecting minute particles of carbide which are only visible at the highest powers of the microscope will easily be appreciated by those who have carried out similar investigations.

Miller[6] apparently held the view that intergranular corrosion was produced by attack on the carbide itself, and to account for this postulated that iron carbide was first precipitated, and that this was gradually converted into chromium carbide, the steel concurrently losing its susceptibility.

It was generally believed, however, that the precipitated carbide consisted mainly of chromium carbide, and there seems little doubt now that this is the case. Data obtained by Westgren[7] and his collaborators showed that the cubic carbide Cr_4C,* in which up to about 25% of the chromium could be replaced by iron, existed in high chromium stainless steels, and one may probably assume that a similar carbide will still be formed if about 10% nickel is added to the high chromium steel. Schafmeister[8] separated the carbide from the disintegrated residue of an " 18-8 " steel which had suffered intense intergranular attack and found its composition to be

Carbon	Chromium	Iron	Nickel
5·35%	59%	26·4%	1·53%

the balance being hydrated silicic acid. These values show the carbide to be Cr_4C with about one-third of the chromium replaced by iron and nickel and, incidentally, they dispose effectively of Miller's theory.

* A more recent paper reports the composition as $Cr_{23}C_6$ rather than Cr_4C ; the difference, however, is immaterial from the point of view of intergranular corrosion.
5 " Prevention of Intergranular Corrosion in Corrosion-Resistant Chromium-Nickel Steels," P. Payson, Trans. Am. Inst. Min. Met. Eng., Vol. 100 (1932), p. 306.
6 " An Investigation of Certain Corrosion-Resistant Steels," J. L. Miller, Carnegie Schol. Mem., Iron and Steel Inst., 1932, p. 111.
7 " On the Structure of the Iron-Chromium-Carbon System," Westgren, Phragmen and Negresco, J. Iron and Steel Inst., 1928, I., p. 383.
8 " Grain Boundary Corrosion and Etching of '18-8' Steels," P. Schafmeister, Archiv. f.d. Eisenhüttenw., X. (1936-37), p. 405.

It is, of course, highly improbable that intergranular corrosion would result from direct attack on such a carbide. Chemists have long been familiar with the fact that high carbon ferrochrome—which consists largely of chromium carbides—is extremely resistant to acid attack, and hence one is led to the conclusion that it is the steel

Fig. 2.—" 18-8 " steel containing intergranular carbide films, deeply etched (10% HCl in alcohol). × 750.

adjacent to the carbide which is attacked, its corrosion resistance having been reduced as a result of the formation of carbide. It is then a natural step to the chromium depletion theory put forward by Strauss, Schottky and Hinnüber[9] and later elaborated by Bain, Aborn and Rutherford,[10] which postulates that the chromium required for the formation of the carbide is taken from the surface layers of the grains where precipitaction occurs, these surface layers being thus largely depleted of their chromium content. The fact that intergranular attack removes considerably more than the precipitated carbide is obvious from the microscopical examination of susceptible samples which have been deeply etched by dilute acids. As is evident from Fig. 2, the grain boundary attack cuts a trench obviously wider than any membrane of precipitated carbide. Bain and his colleagues[10] also showed that the loss of weight of a susceptible sample during complete disintegration in the acid copper sulphate re-agent was greater than could be accounted for by a carbide of any suggested composition. Finally, positive evidence of the existence of the depleted band was obtained by Schafmeister[8], who determined the relative amounts of iron, chromium and nickel taken into solution when samples of steel containing 18·0% chromium, 8·8% nickel and 0·22% carbon, which had been reheated for two hours at either 700°, 725°, 750° or 775° C. were subjected to corrosive attack by cold saturated sulphurous acid for a period of ten days. The attack was entirely intergranular. The results obtained are given below, the amounts of each metal being expressed as a percentage of the total amount of the three metals found in solution.

Metal	Re-Heating Temperature			
	700°	725°	750°	775°
Cr.	9·63	9·7	8·7	10·3
Ni.	7·9	6·7	8·4	8·3
Fe.	82·4	83·5	83·4	81·5

9 " The Separation of Carbide from Non-Magnetic Stainless Chromium-Nickel Steels during Annealing," Strauss, Schottky and Hinnüber, Z. Anorg. Allg. Chem., Vol. 188 (1930), p. 309.
10 " The Nature and Prevention of Intergranular Corrosion in Austenitic Stainless Steels," E. C. Bain, R. H. Aborn and J. J. B. Rutherford, Trans. Am. Soc. Steel Treat., XXI. (1933), p. 481.

These values must represent substantially the composition of the metal dissolved during attack.

On the basis of the chromium depletion theory, one may visualise the precipitation of carbide at, for example, 600° C., proceeding in the following manner in a homogeneous austenite supersaturated with carbon and obtained by rapidly cooling an " 18-8 " steel from a temperature high enough to take all the carbon it contains into solution. The carbon atoms existing close to the grain boundaries will precipitate first owing to the greater atomic activity in these regions, and will take the chromium they require from the austenite in their immediate neighbourhood. The precipitation will reduce the carbon content of the surface layers of the grains to the saturation value at 600°. Further carbon atoms will immediately diffuse into these surface layers from the supersaturated grains which they enclose ; on arriving at the grain boundary, these carbon atoms will also precipitate as carbide, removing more chromium atoms from the surface layers. Meanwhile, chromium atoms will also start to diffuse from the interior of the grains to the depleted surface layers, but the rate of diffusion of these atoms is very much slower than that of the carbon atoms. At least two reasons may be suggested for this. The chromium atoms replace iron atoms in the space lattice, and hence in their case diffusion presumably occurs by substitution, whereas the smaller carbon atoms occur interstitially, and may therefore be expected to move through the lattice with less hindrance ; secondly, the steel is supersaturated with carbon at the temperature in question but not with chromium.

The above picture indicates that the chromium content of the surface layers will decrease with time at 600° until it reaches a minimum—a considerable part of the carbon in excess of the solubility limit at that temperature having then been precipitated—and will thereafter slowly increase as a result of chromium diffusion. Susceptibility will concurrently increase to a maximum and then diminish, being finally removed completely. A temperature of 600° has been used for this illustration, but a similar sequence will hold at somewhat higher or lower temperatures with the exception that the time scale will be shorter in the former case and longer in the latter as a result of diffusion proceeding more rapidly as temperature increases. It will be obvious, however, that the time factor is of the greatest importance not only in laboratory tests to determine the susceptibility of different steels, but also in the industrial application of the latter ; this aspect will be considered more fully later.

The chromium depletion theory appears to explain satisfactorily most of the phenomena, connected with intergranular corrosion, observed in laboratory tests or in the practical use of the steels, and it will be adopted as a working hypothesis in the discussion which follows. It should be noted, however, that there still appear to be doubts in certain quarters as to the validity of the thory and that other theories have been proposed to account for the observed facts. It was noticed in early investigations that samples of " 18-8 ' steels often became somewhat magnetic when they were put into a susceptible condition. It was thought that the austenite transformed to ferrite at the grain boundaries either initially (due to greater atomic activity in these areas) and thus caused carbide precipitation, or as a result of the latter, the austenite thereby being depleted of carbon, one of its stabilising elements. In either case, the ferrite was assumed to be less resistant to corrosive attack than the austenite from which it was formed and thus to be the cause of intergranular breakdown, though why ferrite should be less resistant to corrosive attack than austenite of the same composition (except possibly for some slight loss of carbon) is not evident. Later investigations showed, however, that intergranular attack could occur in alloys of much higher nickel content which remained non-magnetic when made susceptible, and that susceptibility could be produced in " 18-8 " alloys at temperatures below those at which the material became magnetic. Thus, Fig. 3 reproduces results obtained by Bain, Aborn and Rutherford[10] on samples of an " 18-8 " steel, containing 0·08% carbon, which were held for 1,000 hours at temperatures between 400° and 800° C., tests being carried out at intervals of about 20° C. Intense intergranular susceptibility was produced between 540° and 600° C., but the samples so heated did not become magnetic. It was obvious therefore that ferrite was not the cause of intergranular attack, and that its occurrence in certain susceptible steels was merely incidental to the local changes in composition which resulted in susceptibility.

In spite of the knowledge that intergranular attack could occur in steels which were non-magnetic, one still finds the suggestion that the production of ferrite at the grain bounderies is a determining factor. Thus, Becket still wrote round this idea in 1938[11] ; he also suggested another theory, put forward previously by Kinzel[12], that the finely divided state of the carbides—by analogy with troostite—together with internal stresses and electrochemical effects were responsible for intergranular corrosion rather than chromium impoverishment. This theory, which appears to be supported only by somewhat superficial analogies, does not seem very satisfying, particularly in view of Schafmeister's results, nor does it appear to explain adequately why more prolonged heating at, for example, 700° C., removes entirely the susceptibility developed after a shorter period of heating while leaving the precipitated carbide in situ. On the basis of the chromium depletion theory, slow diffusion of chromium from the interior of the grain, thereby raising the content in the depleted areas to a safe level, provides a reasonable explanation, but the agglomeration to some extent of the fine carbide particles which also occurs, would seem inadequate to explain complete immunity from intergranular attack if the latter was due mainly to electrochemical action between carbide and metal.
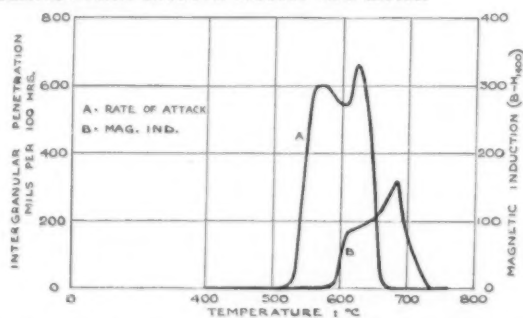

Fig. 3.—Intergranular attack and magnetic induction in " 18-8 " steel reheated 1,000 hours at the temperatures indicated.

Miller[6] objected that the precipitation of chromium carbide involved diffusion of chromium, and if this could occur in a few seconds at 650° C., causing a depletion of chromium within certain localised areas, further migration of chromium to enrich these depleted areas should also occur. But surely it is a question of degree. The probability of the formation of chromium carbide was examined by Bain, Aborn and Rutherford[10], and one cannot do better than quote their words :

"Statistically, well over one quarter of the atoms on every other plane in the solid solution are chromium atoms ; on certain lines extending through the alloy, every other atom is a chromium atom. In other words no chromium atom (on the average) is separated from its nearest chromium neighbour by more than one iron atom, although a representative group of 1,000 atoms of the 0·10% carbon, " 18-8 " alloy is comprised as follows :

Carbon	5 atoms
Nickel	75 ,,
Chromium	190 ,,
Iron, etc.	730 ,,

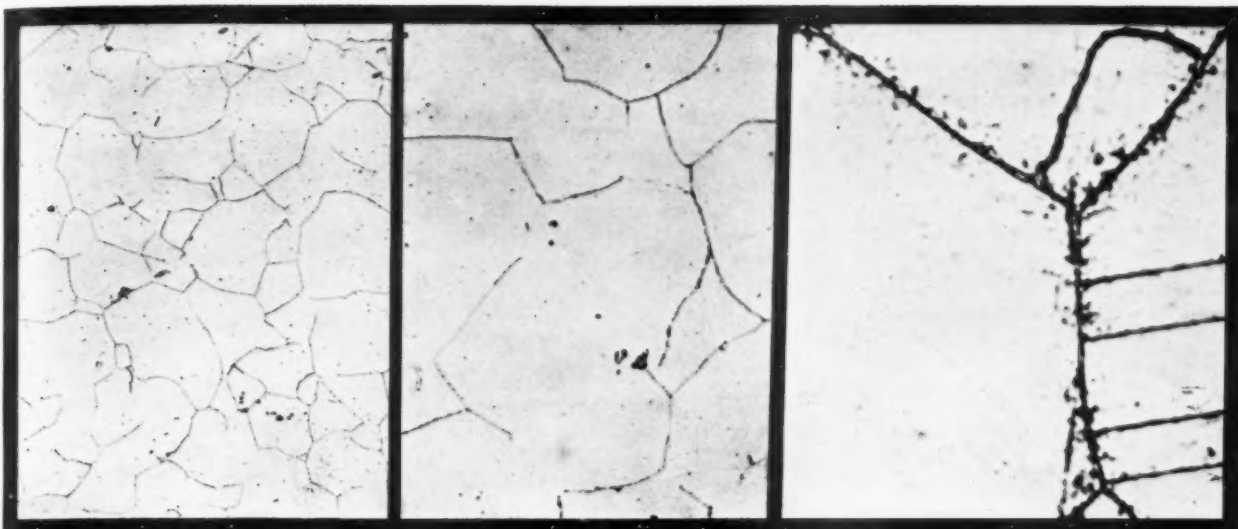Hence the building up of a chromium-rich carbide crystallite is not difficult if the preference for carbon to

Fig. 4.—" 18-8 " steel heated for about two minutes at 700° C., lightly etched with 10% HCl in alcohol. × 150.

Fig. 5.—" 18-8 " steel heated for about two minutes at 700° C., lightly etched with 10% HCl in alcohol. × 750.

Fig. 6.—Carbide particles in grain boundaries of " 18-8 " steel reheated at about 650° C. ; etched Murakami's reagent. × 3,000.

unite with chromium instead of iron is marked, as, indeed, it is known to be."

Although some slight migration of chromium atoms may occur during the formation of the carbide, the distances through which these atoms must move is almost negligibly small compared with the distances which must be traversed by chromium atoms coming from the interior of the grains to enrich the depleted boundary layers.

Tests for the detection of susceptibility to intergranular corrosion fall into two broad groups :

(1) those to determine whether a given sample is in a susceptible condition,

(2) those whose object is to show whether a given material will or will not develop susceptibility after being subjected to certain treatments or fabrication processes.

Detection of susceptibility may take the form of microscopic examination or of a controlled corrosion test, the latter being generally preferable. In the former case, dependance is often placed on the presence or absence of a structure, i.e., a carbide network, which may be assumed to be likely to cause intergranular attack, and it should be realised that it is not always infallible. A steel may contain a distinct carbide network and yet not be susceptible to intergranular attack if it has been held long enough, at the temperature causing precipitation, for adequate diffusion of chromium to occur. In such cases the carbide may exist as more or less balled up particles outlining a cell structure rather than as a continuous membrane, but again the fact that balling up has occurred to an appreciable extent is not an infallible indication that susceptibility has been removed. Murakami's reagent darkens the carbide, leaving the groundmass unaffected, and hence shows definitely whether carbide is present or not. The precipitated carbide, however, may be in the form of extremely fine particles, necessitating careful examination at the highest powers to detect their presence, and yet be sufficient to cause appreciable intergranular attack. There is much to be said therefore for etchants of an acid character which attack the depleted band on each side of the carbide membrane, and thus produce a " black line " effect of greater width than the membrane, and hence more easily visible than the latter. If etching conditions are so controlled that practically no attack develops on the normal part of the grain, they then produce a clear picture of the boundaries which are subject to intergranular attack. For the plain chromium-nickel steels, a 10-15% solution, by volume, of concentrated hydrochloric acid in alcohol is a good reagent, its only disadvantage being that the etching time is rather long, e.g., 15 minutes or so. Etched in this way, the depleted

bands in a susceptible steel show up very plainly against a practically unattacked background because the correctly treated steel requires a much longer period of etching— three hours or more—to develop its structure. Figs. 4 and 5 reproduce the appearance of a susceptible steel (actually the same as that shown deeply attacked in Fig. 2) etched in this manner, and one may note the easy visibility of the etched pattern at so low a magnification as X150. For comparison, Fig. 6 shows the fine carbide particles in a markedly susceptible steel after etching with Murakami's reagent ; they require a much higher magnification to make them easily observable.† In passing one may note that the carbide membranes (and hence the depleted bands) are not quite continuous in Figs. 2, 4 and 5, probably because the steel in question had been heated for only a very brief period (about two minutes) at 700° C. ; where carbide has not precipitated, the grain boundary is almost invisible in the lightly etched sample.

The rather long period of etching required with this reagent is a disadvantage which becomes more pronounced when complex steels, containing other alloys, such as molybdenum, copper, silicon, which increase acid resistance, are under investigation. Its action may be speeded up by additions of concentrated nitric acid or ferric chloride, about 5% by volume of the acid or 5% by weight of the chloride being suitable quantities. Other acid etchants have been used by different investigators with greater or less success. What should be avoided is the use of a very energetic reagent which rapidly etches the normal steel and therefore tends to mask the intergranular attack.

Electrolytic etching has been proposed by a number of investigators as a method which can readily be controlled so as to produce the desired effect. Various solutions can be used for this form of etching, and among them a 10% solution of sodium cyanide has received considerable support ; the 10% alcoholic solution of hydrochloric acid, mentioned above, is also suitable, its action on the steel being intensified by the electric current. Schafmeister recommended a 10% solution of ammonium nitrate, which, he states, allows both the carbide and the depleted boundaries to be shown ; its action is readily controlled so as to obtain the desired degree of etching, and there is no danger of poisonous fumes being produced during its use. Schafmeister also emphasised the disadvantages of powerful acid-etching *media* which attack the normal steel rapidly, and hence do not allow proper control of the etching process. (To be continued)

Manganese in the Steel Industry

The problem of obtaining enough manganese for use in the manufacture of steel is presented when international relationships are disturbed and becomes serious when customary supplies are cut off. Reasons for the use of manganese are briefly reviewed and several aspects of the subject are discussed including consumption of the element, distribution of the ores, manganese-containing products available to the steel industry and economies possible in their use are suggested. While reduction of the amount of manganese in specifications is possible in some instances, the change would involve either a lowering of the physical properties of the steel or the use of other materials, as well as a change in practice likely to involve some delay and increased cost of final product.

NATURALLY occurring oxides of manganese have been employed since ancient times as agents for decolorising glass; but whereas the ancients had metallurgical use for the ore, it is at present indispensable in the manufacture of steel, and no acceptable or adequate substitute has yet been discovered nor is any in prospect. According to Rogers,[1] manganese is used in steel for two reasons: First, because of its favourable effect in workability, and second, for its ability to improve the product. Good workability enables the steel to undergo forging, rolling and other processes without being ruptured or otherwise damaged. Improvement of the product refers to the ability of the steel to perform satisfactorily under various operations under service conditions. To these two reasons Ellicott[2] adds a third—the meeting of specifications which demand higher percentages of manganese that are necessary to give suitable properties to the finished product.

The beneficial effect of manganese in the reduction of ingots to the desired shape is well-known, and the general reasons are fairly well agreed upon, although there is some controversy regarding details. The action of manganese in taking the sulphur from iron sulphide to form manganese sulphide appears to be of major importance. The nature of the first of these sulphides is such that at a certain stage of cooling it works out between the grains in the steel and surrounds them with thin, low-melting envelopes of iron sulphide; whereas the second agglomerates into small globules dispersed throughout the metal. A piece of steel which contains iron sulphide tends to fall apart during forging because of the lack of cohesion between the grains of metal, whereas one in which the sulphur is present as manganese sulphide does not exhibit this undesirable behaviour.

The foregoing does not fully explain why manganese eliminates the hot shortness of steel and permits it to be rolled without difficulty. There appears to be little doubt that the amount of oxygen present also has an effect, and some investigators consider it to be the major influence. A rather comprehensive experimental investigation and analysis of published data by Norris[3] resulted in the conclusion that a steel in which the percentages of oxygen and sulphur are such that the ratio $\dfrac{Mu + 0 \cdot 048}{S + 0 \cdot 130}$ is greater than $6 \cdot 63$ is never red-short; if this ratio is less than $3 \cdot 30$ the sample is always red-short; and if its value is intermediate the heat-treatment of the sample determines the existence of the red-short condition. In this expression the chemical symbols represent the weight percentages of the corresponding elements.

The second reason for using manganese obviously refers to its employment as an alloying element. Manganese is commonly used in steels to impart certain desired properties, but the product is not usually classified as an alloy steel until the content of this element exceeds $1 \cdot 60\%$. An example of such use is the addition to low carbon sheet steel of $0 \cdot 20\%$ more manganese than the $0 \cdot 15$ to $0 \cdot 20\%$ required to ensure good behaviour in rolling. The additional amount eliminates the likelihood of a bad surface after a drawing operation and thus improves the quality of the finished product.

The two reasons outlined—to ensure proper ductility under hot working at all temperatures and to improve the character of the steel for specific purposes—constitute the arguments for using manganese. They are not the only reasons, however, as the presence of manganese oxide in the furnace slag must be considered during melting operations, so that a difference in the amount of manganese charged presumably demands somewhat changed procedures in handling the furnace. Because of the lack of agreement concerning the function of manganese in the furnace, this aspect is not considered further; references to this subject, however, may be found in recent articles by Lawrie,[4] Diepschlag[5] and others.

Consumption of Manganese

The total consumption of manganese in the steel industry can be estimated reasonably well, but knowledge of the amounts consumed in the various steel products is less accurate. It is particularly difficult to specify how much material is used to make rolling possible and how much is employed to improve the character of plain carbon steels. A rough idea may be gained by noting the approximate amount of manganese used in all classes of steel and arbitrarily assigning some fraction as being essential to ensure proper rolling characteristics. Probably because so often manganese is added in greater quantities than will just suffice to ensure suitable working properties in the steelworks, little information is available as to the minimum amount necessary for this purpose. Furthermore, the percentage is not the same in all plants. A modern mill with first-class heating facilities can roll material containing slightly less manganese, other factors remaining the same, than can be handled with an older type mill with poor heating arrangements. As the present problem primarily concerns the consumption of manganese containing additional materials, estimates of amounts used will refer only to the manganese added at the end of the heat.

A rimming steel may be rolled consistently if it contains $0 \cdot 18\%$ manganese,[6] or perhaps even a little less in some cases. Since the residual manganese in a heat of such steel may be approximately $0 \cdot 10\%$, probably $0 \cdot 08\%$ must be added as a minimum. On the other hand, for some other types of killed steels addition of $0 \cdot 25\%$ manganese above the residual amount may be desirable. For all classes of steel a rough average of $0 \cdot 15\%$ will be assumed. In 1937 the total output of steel ingots produced in the United States was slightly more than 50,000,000 gross tons.[7] In view of the above assumptions the round number is

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1 B. A. Rogers, *Bureau of Mines Information Circular 7162.*
2 C. B. Ellicott, "The Conservation of Manganese": *Am. Iron and Steel Inst. Year Book,* 1918, pp. 25–37.
3 F. G. Norris, "Factors Affecting Red-Shortness": *Jour. Iron and Steel Inst.,* 138, 1938, pp. 75–79.

4 W. B. Lawrie, "The Refining of Metal in the Basic Open-Hearth Furnace": *Jour. Iron and Steel Inst.,* 139, 1939, pp. 257–280.
5 E. Diepschlag, "Das Mangan in der Stahlerstellung" (Manganese in the Manufacture of Steel): *Metallwirtschaft,* 17, 1938, pp. 1299–1302.
6 No manganese is added to Armco ingot iron and low metalloid heats in general. Such heats contain very little residual manganese, they are rolled in a special way to avoid trouble from hot-shortness.

accurate enough for the purpose. On this basis 75,000 tons of manganese was required to make this quantity of steel workable.

The total amount of manganese consumed in the United States in the form of ferro-manganese and spiegeleisen, in 1937, was, in round numbers, 350,000 long tons,[8] of which approximately 320,000 tons was furnished by ferro-manganese and the remainder by spiegeleisen. The assumption of an average loss of 25% in making the additions indicates that about 265,000 tons of manganese actually entered the steel. Of this total amount, about 75,000 tons, or about 28%, was used in making the steel workable. If this conclusion is put in round numbers, the analysis indicates that somewhat less than one-third of the manganese is used for the benefit of the producer of steel and a little more than two-thirds in improving the character of the steel for the benefit of the user.

Relatively little manganese is consumed in products classed as alloys. In addition to the steel containing more than 1·60% manganese, in this group may be included Hadfield steels, containing 11% to 14% manganese, cast steels and cast-irons containing added manganese. This group is not large and for practical purposes may be ignored, as it probably does not consume more than 4% or 5% of the manganese used in the steel industry. The consumption of manganese in Hadfield steels, for example, may not have exceeded 5,000 tons in 1939.

Distribution of Manganese Ores

Although manganese ores occur widely distributed throughout the world and most countries have some resources which might be used in emergency, large scale production is confined to the U.S.S.R., India, the Gold Coast, South Africa, Brazil, Egypt and Cuba, with important contributions from Czechoslovakia, Japan, China and the Unfederated Malay States.[9] It is noteworthy that the United Kingdom and the other great iron and steel-producing countries of Europe (except Russia), as well as the United States and Canada, have to rely almost entirely upon imports from distant countries for their essential supply of manganese ore of metallurgical grade.

The problem of obtaining enough manganese for use in steel manufacture is not difficult in times of peace, it appears, however, when international relationships are disturbed and becomes serious when customary supplies are cut off. This condition arises because in normal times there is an economic advantage in importing available high-grade ores to the neglect of less satisfactory domestic resources. In the United Kingdom manganese ore occurs in North Wales, the West of England, Derbyshire, Warwickshire and Cumberland, also in Scotland and in Ireland. The production of this ore was never large; since 1912 it attained a maximum of 17,456 tons in 1918, after which date it fell to 235 tons in 1928; since then no output has been recorded. For many years practically all the output was obtained in North Wales, where most of the ore contained about 32% manganese.

The British Empire, however, is favourably situated with regard to supplies of manganese ore, the reserves in India, the Gold Coast, Union of South Africa, Malaya and Northern Rhodesia reaching a vast total. Empire counties contribute about one-third of the world's production, and if exports are considered the proportion is approximately twice as great, due to the fact that the U.S.S.R. (the world's largest producer), Czechoslovakia and Japan consume the greater part of their own output.

Excluding the U.S.S.R., Germany is the largest consumer of manganese in Europe, but her deposits of high-grade manganese ore are to-day of little more than his-

torical interest. In 1936 the production of ore containing over 30% of manganese was only 238 tons, and in view of the extent to which the German ore deposits have been studied, the possibility of further manganese ore occurrences of economic importance being discovered is regarded as remote. On the other hand, Germany produces large quantities of manganiferous iron ore of which she has considerable resources. The manganese content of her output of manganese ore and manganiferous iron ore is about 200,000 tons, whereas her manganese requirements are about 400,000 tons annually,[10] considerable quantities therefore must be imported.

In recent years Germany has made determined efforts to utilise not only low-grade ores but also manganiferous slags and scrap. The low-content manganiferous ores were at one time reduced at a low temperature resulting in the separation of the iron and the formation of a manganese-rich slag, and attempts were made to manufacture ferro-manganese from this slag. A new process[11] was developed, however, which produces ferro-manganese from the low-content German ore by first smelting the ore into spiegeleisen in a blast furnace by the usual methods. Part of the spiegeleisen is then treated in a basic converter and the other part in an acid converter. The two manganiferous slags are mixed for a blast furnace charge in such quantities that the silica content of one is neutralised in the lime content of the other. The ferro-manganese obtained is claimed to be similar in composition to the product resulting from the smelting of high-grade imported ores. Domestic slags such as those obtained from ferro-manganese, spiegeleisen and Siemens-Martin furnaces also assist in meeting Germany's manganese requirements. Spiegeleisen slag has a manganese content of 10% to 13%; that of Siemens-Martin slag from 7% to 14%. Figures[12] indicate that low-grade ores, slags and scrap are used to a considerable extent by the German steel industry to supply the necessary manganese in steel manufacture.

Manganese-bearing ores in the United States are known to occur in about 300 districts scattered throughout 35 states. Many of the deposits are small, containing only a few hundred or a few thousand tons, but there are some which contain millions of tons of ore. In spite of the wide distribution of manganese-bearing ores, only a few localities are of commercial importance in normal times, but the possibility of expanding domestic production was actually demonstrated during the Great War when the annual production from United States ores rose from about 4% to approximately 35% of the total consumption of ferro-manganese and spiegeleisen. Surveys of the manganese situation, however, have definitely established the fact that the tonnage of high-grade manganese ore in the United States is relatively small; large scale production of manganese, therefore, is possible only through benefication of low-grade material.

Deposits of low-grade ore are being examined to determine their size and possibilities as sources of manganese on a tonnage basis; at the same time benefication processes are being developed and perfected with the object of using these low-grade ores. Head[13] presents the results of studies of samples from low-grade ores originating in Utah and other Western States. The manganese content of typical low-grade ores varies greatly, ranging from 1% to between 5% and 30% or more in numerous occurrences throughout the West. Although some of these ores are marketable as mined for blast-furnace purposes, their greatest potential value lies in the possibility that their manganese content may be "graded up" by the production of high-grade concentrates suitable for making ferro-manganese.

7 R. H. Ridgway and H. W. Davis, "Iron Ore, Pig-Iron, Ferro-Alloys and Steel": *Minerals Year Book*, 1938, pp. 479-523.
8 R. H. Ridgway and H. W. Davis, "Manganese and Manganiferous Ores": *Minerals Year Book*, 1938, pp. 525-539.
9 A. W. Grooves, "Manganese" (Second Edition): Report published by the Imperial Institute.

10 K. Hatzfeld, "Die Aufgaben des Bergbau im Ruhmen des Vierjahresplan": Der Bergbau, 1937, 50, p. 4.
11 *Chem. Age*, Lond., 1937, 36, *Met. Sect.*, April 3, p. 19.
12 G. Einecke, "Die deutchen Eisenerzlagerstätten und ihre Nutzungsmöglichkeiten": *Z. Ver. Dtsch. Ing.*, 1935, pp. 1099-1110.
13 R. E. Head, "Physical Characteristics of Some Low-Grade Manganese Ores": *Bureau of Mine's Report of Investigations* 3560, 1941.

Manganese-containing Products Available to the Steel Industry.

Various manganese products are available for use in steelworks. In the order of their manganese content, Rogers gives them concisely as electrolytic manganese and manganese metal; ferro-manganese and silico-manganese; spiegeleisen and silico-spiegel; and manganiferous pig-iron.

Electrolytic manganese is a recent product,[14] with an actual manganese content probably in excess of 99·9%, and with practically no phosphorus and very little sulphur. Fortunately it can be made from relatively low-grades ores, but at present production is not on a scale to furnish large amounts to the steel industry. So far the cost of the material has been somewhat higher than an equivalent amount of manganese in the ferro-alloy form. Experiments[15] have indicated that the electrolytic product behaves essentially the same as ferro-manganese in open-hearth steel. Use of this product would logically be in the comparatively small tonnage of low-carbon, high-manganese products, where it would have an economic advantage because of the furnace time saved in not having to reduce the carbon in the heat to compensate for that added with the ferro-manganese.

Manganese metal containing 95% to 98% of the element, is a thermit product that hitherto has been unable to compete economically with ferro-manganese. The commercial product contains about 1% of either silicon or aluminium, or both.

Ferro-manganese is an alloy of approximately 80% manganese with about 16% iron and carbon up to about 6% or 7%, depending on the method of production. It is the material made from high-grade manganese ores or concentrates, and it is probably the most convenient form in which to add manganese. To avoid the addition of carbon to low-carbon, high-manganese steels an electric furnace product containing much less carbon than the usual blast-furnace alloy is sometimes used. However, consumption of the electric furnace product is small; its cost is probably twice that of the alloy made in the blast-furnace. For certain killed steels, silico-manganese, with the approximate composition 65% to 70% manganese, 12% to 25% silicon and 1·2% to 2·5% carbon is preferred. Ferro-manganese has the distinct advantage over other forms of manganese alloys that considerable percentages of manganese—perhaps as much as 1·5%—can be introduced in the ladle without cooling the steel excessively.

Spiegeleisen is the other form of alloy commonly used for introducing manganese. It usually contains about 20% of the element; the remainder of the alloy is made up of iron together with about 5% carbon and perhaps 0·5% silicon. Silico-spiegel, which contains about 25% to 30% manganese and 7% to 8% silicon, finds limited use in the industry. Spiegeleisen is a satisfactory substitute for the ferro-alloy in making additions of manganese, provided that the accompanying elements, such as carbon and phosphorus, are consistent with the grade of steel being made. For example, speigeleisen as a recarburiser for rail steel replaces pig-iron as a source of carbon and ferro-manganese as a source of manganese. Difficulties resulting from cooling the steel by too large an amount of cold spiegeleisen, either in the furnace or in the ladle, may be avoided by pre-heating or pre-melting the added material.

The manganiferous pig-iron with perhaps 5% manganese can be used for additions when the amount required is not too great or may be supplemented by the use of ferro-manganese. For additions in the ladle this material may be used in the molten condition.

Economising in the Use of Manganese

In view of the fact that most steel-producing countries must import a substantial proportion of the necessary manganese, several schemes have been presented for reducing the amount of this element required for the production of satisfactory steel, and in the following notes suggestions have been classified.

Economy in Use of Amount of Manganese.—This is intended primarily to cover the consumption of manganese in steel used for purposes for which material of lower quality would serve equally well. A survey of the uses to which certain products are put would probably result in some saving. The use of slightly higher carbon contents no doubt would offset the lower percentages of manganese in certain products without detriment to structures in which the material was used. When possible rimmed steel should be substituted for the killed product as less manganese is required in the manufacture of the former.

Substitution of High-grade by Low-grade Manganese.— The methods of economising included in this class involve not so much a saving in manganese metal as a change in practice to make use of available material. In the last Great War it was frequently necessary to substitute speigeleisen for ferro-manganese, while manganiferous pig-iron was often substituted for spiegel in recarburising work. Herty[16] has proposed the use of a silicon-containing spiegeleisen of the composition 20% manganese, 4% silicon, 4·25% carbon, and the remainder iron, and also of a special alloy containing 30% manganese, 5·5% silicon and 2·5% carbon, both of which can be manufactured from United States ores. Such agents could not be used for all types of steel but could replace a large proportion of the ferro-manganese and silico-manganese now being used. The heat of reaction of the silicon present in this allow should compensate somewhat for the chilling effect of the addition and permit its use in the cold condition in greater quantities. Furthermore, because of the action of silicon on the oxygen in the bath the losses of manganese should be less than for ordinary spiegeleisen.

Substitution of other Deoxidising Agents.—It must be emphasised that manganese is more important for its ability to render ineffective the bad characteristics of sulphur in rolling and forging operations than for its deoxidising power. There are a number of agents, of which silicon is an example, that are more effective deoxidisers than manganese, but silicon is not a substitute for manganese because it does not remove the harmful effects of sulphur. Of the various substitutes suggested, zirconium and titanium appear to have the greatest possibilities, although both seem to be excluded for this purpose in rimming steels, as they would produce a killed steel before taking care of the sulphur. However, the cost of either ferro-alloy would be high upon such a basis as point-for-point substitution for manganese, and perhaps more difficult to obtain.

Substitution of other Strengthening Elements.—The manganese used as an alloying element can obviously be replaced, with satisfactory results, by other elements, such as nickel, chromium, molybdenum or silicon. But as the manganese-containing steels have been developed and utilised partly because of their relatively low cost in comparison with other low-alloy types, manganese will continue to be used until its cost rises considerably. There seems little doubt, however, that in an emergency such replacements could be made; but consideration should be given to the fact that, in the majority of instances, a steel making country must import the bulk of these elements, and in an emergency the difficulties may become as acute as with manganese.

Modification of Furnace Practice to Reduce Manganese Used.—The conservation of manganese in open-hearth

14 W. L. Hammerquist, "Electrolytic Manganese: A New Metallurgical Raw Material": *Steel*, 105, 1939, pp. 42–45.
15 H. M. Banta, Jones & Laughlin Steel Corporation, *Research and Development Div.*, Rept. 90-40, 1940.

16 C. H. Herty, Jr., *Bureau of Mines Rept. of Investigations* 3107, 1931.

furnace operation has been commented upon by many steel makers. In certain basic furnace procedures, for instance, the employment of high-manganese pig-iron, or the addition of manganese to the charge in some other form, makes possible the retention of a high-residual manganese and thus effects a reduction in the amount of ferro-manganese to be added at the end of the heat. The

17 Bardenheuer, Peter, and Thanheiser, " Methods of Saving Manganese in the Operation of Siemens-Martin Furnaces ": *Mitt. Kais. Wilh. Inst. Eisenforsch.,* **20,** 1938, pp. 67-75.

18 Bardenheuer and Henke, "Preventing the Loss of Manganese in the Open-Hearth Process ": *Mitt. Kais. Wilh. Inst. Eisenforsch.,* **21,** 1939, pp. 243-260.

use of small slag volumes and delay in adding limestone are recommended[17] for this purpose. Bardenheuer and Henke[18] describe a number of procedures in handling molten steel which they claim permit small savings of manganese ; an example is the tilting of the ladle in such a way as to avoid turbulence as the steel is being teemed in. Other possibilities that might be considered are the reduction of sulphur in the pig-iron (hot metal) by means of the soda ash procedure and its elimination from the incoming fuel. The smaller amount of sulphur introduced into the furnace should require less manganese to render it harmless.

Examination of a High-Sulphur Free-Cutting Steel Ingot

By E. Gregory, Ph.D., M.Sc., F.I.C., and J. H. Whiteley, F.I.C.

An ingot of steel of high sulphur content was subjected to a detailed examination in regard to heterogeneity, and an examination of the inclusions in it was made. The results are reported in a paper to be presented at the Autumn General Meeting of the Iron and Steel Institute. This is an abridgement of an advance copy.

THE main features of this steel, which experience has proved to possess excellent free-cutting and other properties, is its exceptionally high sulphur content The composition generally aimed at lies between the following limits :—

Carbon	0·08-0·12%
Silicon	0·04% max.
Sulphur	0·40-0·50%
Phosphorus	0·035-0·045%
Manganese	1·00-1·20%

In view of the abnormally high sulphur content of this steel, it was considered that the examination of an ingot of this quality might prove of interest and perhaps shed some light on the heterogeneity of steel ingots generally. The selected ingot was taken from a cast made in a basic-lined open-hearth furnace of 65 tons capacity, and the cast analysis (H952) was as follows :—

	C, %	S, %	P, %	Mn, %
Pit test (1)	0·08	0·466	0·043	1·01
(2)	0·09	0·480	0·043	1·02
Test ingot:—Billet No. 2	0·08	0·462	—	1·07
,, 4	0·08	0·466	0·039	1·07
,, 6	0·09	0·470	—	1·10
,, 8	0·08	0·482	0·044	1·05

Part 1.—Investigation of the Heterogeneity of the Ingot.

The experimental evidence recorded in this part of the paper by Dr. E. Gregory indicates that the degree of segregation is less than might be expected, and shows no greater relative degree of segregation in regard to sulphur than in a steel having a " normal " sulphur content. Thus, the analytical results show a variation in sulphur content from 0·415 to 0·491%. Taking the mean as 0·453%, this indicates a degree of segregation amounting to ± 8·4% of the actual average sulphur content. In a steel containing, say, an average of 0·05% of sulphur, this degree of segregation would result in areas containing 0·054 and 0·046% of the element, an indicated degree of segregation which is often much less than that found in practice. It would seem, therefore, that the actual mechanism causing segregation is the same in both high- and low-sulphur steels.

It is of interest to note the relatively slight degrees of phosphorus and manganese segregation, a somewhat unexpected result.

The greatest degree of segregation is in regard to oxygen, and, curiously enough, this seems to be entirely independent of the manganese, but there is some indication that the oxygen and sulphur segregations are inverse to each other. From this it may be concluded that sulphur, as well as manganese, plays an important part in the ultimate degree of deoxidation.

So far as the nitrogen contents are concerned, the degree of heterogeneity is relatively small. The hydrogen segregation is definitely more marked than that of the nitrogen, but bears no relation to the oxygen segregation, indicating that in the presence of iron the equilibrium position for the reaction $2H_2O \longleftrightarrow 2H_2 + O_2$ at the temperature of freezing steel lies well to the right, whence it follows that the oxygen and hydrogen contents are independent of each other and proportional only to their partial vapour-pressures at the actual period when solidification occurs.

At positions H and near the outside of the ingot the inclusions, both large and small, are apparently quite homogeneous, whereas the larger inclusions in the interior of the ingot possess duplex structures ; in some cases these inclusions have the appearance of eutectics and in others the lighter constituent is decidedly dendritic in nature. From the results of the analyses given in Table I it is clear that, so far as the larger inclusions are concerned, their homogeneity, or otherwise, is largely a question of oxygen contents. When the oxygen content is low the inclusions apparently consist of a single constituent, but with higher oxygen contents their structures are duplex in nature. From this it may be inferred that the lighter constituent in the micrographs shown is an oxide, or an oxide-sulphide complex relatively rich in oxygen, and the darker constituent a solid solution of iron and manganese sulphides containing little or no oxygen. In the regions in which large homogeneous inclusions are found it may be suggested that practically the whole of the oxygen is contained in the ferrite matrix in which the inclusions are embedded, since it must be appreciated that the oxygen determinations were conducted on pieces of steel the dimensions of which were very large compared with those of the contained inclusions. On the other hand, since duplex structures are apparently associated with general high oxygen contents, it may be assumed that the actual oxygen contents of these inclusions exceed the values indicated in Table I.

TABLE I.
ANALYSES AT THE STANDARD POSITIONS IN THE INGOT.

Position.	C, %	Si, %	S, %	P, %	Mn, %	O, %	N, %	H, %
B	0·07	0·005	0·415	0·042	1·03	0·057	0·0023	0·00036
A	0·08	0·009	0·491	0·044	1·02	0·014	0·0022	0·00037
F	0·065	—	0·483	0·041	0·99	0·046	0·0028	0·00059
C	0·08	—	0·475	0·044	1·04	0·052	0·0025	0·00069
F₁	0·07	—	0·430	0·041	1·04	0·014	0·0029	0·00057
A₁	0·07	—	0·476	0·042	1·03	0·012	0·0020	0·00040
G	0·075	0·005	0·480	0·042	1·02	0·040	0·0025	0·00042
D	0·08	—	0·474	0·044	1·01	0·044	0·0021	0·00052
G₁	0·08	—	0·452	0·042	1·05	0·044	0·0023	0·00047
H	0·08	Trace	0·478	0·044	1·00	0·013	0·0026	0·00041

Notwithstanding the duplex nature of such inclusions, they appear to exert no detrimental effects on the rolling properties of the steel. Indeed, it may be stated that rolling difficulties, within the author's experience with steel of the quality under consideration, are definitely less than with steels of the more normal high-sulphur type containing lower proportions of sulphur. In view of the fact that the inclusions in the present ingot exist in spherical or globular forms instead of as films along the crystal boundaries, the excellent rolling properties of this steel are not unexpected. During the subsequent rolling of these ingots the essential change which occurs in the nature of the duplex inclusions is their elongation into threads. The duplex structure is often retained in the rolled bloom, billet or bar, although no evidence has been obtained, after rolling, of the persistence of dendritic or eutectic structures.

Unfortunately, at the moment, there appears to be no absolutely reliable method of analysing the inclusions in order to determine definitely their constitutions, but the possibilities of electrographic micro-chemical analysis and of spectrographic analysis have not been overlooked, and these methods are receiving attention. Meanwhile, the problem of identifying the constituents of the inclusions has been tackled from the microscopical point of view by Mr. J. H. Whiteley, whose findings are given in Part II below.

Part II. — Examination of the Inclusions in the Ingot.

Three pieces weighing about 1½ oz. each were received for the investigation of their inclusion contents. The positions in the ingot from which they were taken are stated in Table II; the letters refer to the analytical positions that have been standardised by the Committee on the Heterogeneity of Steel Ingots.

TABLE II.
POSITIONS FROM WHICH SAMPLES WERE TAKEN.

Piece No.	Position Where Cut.
1	Near edge along the GDG₁ axis of the ingot.
2	Near G—i.e., about half-way to the centre.
3	Close to H—i.e., at the base of the head.

A preliminary survey of prepared sections under the microscope showed that all three pieces contained very numerous dove-grey inclusions. For the most part they were rounded in shape, but their sizes varied rather widely. Generally these particles were opaque, though occasionally one was observed to be translucent, and in every such instance the internal reflection had a reddish tint. In view of the high sulphur content of the steel there could be little doubt that these inclusions, both opaque and translucent, were a sulphide, and since they had the usual colour of MnS were provisionally considered to be that compound. Yet not entirely so, for under a high magnification some were seen to be composite in character, having at their margins films of a dark glassy substance.

Besides these very numerous MnS inclusions another type was present, although in much less quantity. Inclusions of this kind were invariably globular in shape and often complex in structure. Some were outstandingly large, a diameter of 0·2 mm. being by no means uncommon. Embedded in the ground-mass of many of these globules,

and giving them a striking appearance, were several rounded opaque particles of exactly the same colour as the MnS inclusions. This complex type of inclusion occurred by far the most frequently in sample No. 2; it was seldom encountered in samples Nos. 1 and 3, and, in order to give some idea of this difference, the approximate number per cubic inch in each sample was calculated from the number visible at a magnification of 100 in an area of ⅕ in. square. The results are recorded in Table III, together with the oxygen contents of the samples as determined by Dr. W. H. Hatfield. It will be seen that there is a definite correspondence between the two sets of figures. The large amount of oxygen in sample No. 2 was apparently connected with the high content of complex globules—as further evidence, to be given later, will also indicate—and, since similar large percentages of oxygen were found at all the interior standard positions except F₁ (see Table I), the inference may be drawn that these globules were equally numerous throughout the central part of the ingot.

TABLE III.
COMPLEX PARTICLE COUNTS AND OXYGEN CONTENTS.

Sample No.	Composite Particles Observable at × 100.	Oxygen in Sample, %
1	27	0·014
2	6,000	0·040
3	8	0·013

The distribution of the MnS particles in all three samples was fairly uniform, except that here and there a tendency to a network arrangement was noticeable. The inclusions in the steel near the skin of the ingot were smaller, but more numerous than towards the centre. There was a similar difference between samples Nos. 1 and 3. Evidently, therefore, the sulphide inclusions increased in size as the rates of solidification and subsequent cooling became slower, a common feature in blow-hole-free ingots. This growth, which may have been the result both of coalescence and of deposition from solution, is discussed by the author.

Following the study of coalescence of sulphides, the specimens were etched with a cupric reagent in order to ascertain whether any connection existed between their heterogeneity and the tendency to a network arrangement exhibited chiefly by the smaller MnS inclusions. For this purpose Le Chatelier and Dupuy's reagent was applied, and in each case a normal cored structure was revealed, with no outstanding heterogeneity. MnS particles were still plainly visible, and it was found that the occasional partial network formations were situated outside the cores, while the largest of the sulphide inclusions always occurred within them. Another three sections were then prepared and etched with the same reagent. This time two or three highly segregated areas were disclosed in both samples Nos. 2 and 3. Although no complex globules were observed in these areas, they were manifestly richer in sulphide than the surrounding metal. Many of the inclusions were very large, light in colour and had a broken appearance, thus suggesting the presence of a considerable amount of FeS. On closer examination this was seen to be the case. Heavy inclusions of the brittle yellowish compound were found, and in addition there were numerous " duplex " particles composed of both FeS and MnS.

Having ascertained that FeS was present in quantity in the heavily segregated areas in the ingot, a lengthy examination was then made for this inclusion in the comparatively homogeneous parts, but, except for one mixture particle in sample No. 1, none was discovered. Seeing that the Mn/S ratio was low in the steel, the occurrence of FeS occasioned no surprise, for there was good reason to believe that, during solidification, this compound would form the bulk of the sulphide inclusions. Yet, since the manganese content exceeded by about 0·2% the amount required for combination with the sulphur, the whole of the FeS could have been converted to MnS, assuming, of course, that the diffusion of manganese into the segregate was sufficiently rapid. Anyhow, the quantity of FeS in

these areas seemed altogether disproportionate, for elsewhere there was practically none. These considerations led to some experiments which are described. It is shown that, on heating the steel to within the liquidus-solidus range, the MnS inclusions were replaced by groups of minute particles containing much FeS. In cooling, two distinct arrangements of these particles occurred, both resembling eutectic formations.

Owing to the presence of local areas rich in FeS, the diffusion of manganese in the steel up to 1,350° C. was investigated. Two effects due to manganese which seemed likely to be informative were employed, the first being its retarding action on the tendency of pearlite areas to coalesce at their margins. As is well known, the Ar_1 transformation in hypo-eutectoid steels takes place over a short range of temperature, and while the transition continues the borders of the pearlite grains already formed are apt to thicken by the transference of carbide from the areas of austenite still in the vicinity, the deposition becoming more rapid as the manganese content is lowered. With less than 0·40% the process can be so active as to change some pearlite areas in mild steel into massive carbide, even when the specimen is cooled in air. Coalescence in the ingot under discussion was found to be no exception to this rule, for, although the average manganese content was 1·025%, the greater part was in combination with the sulphur at 900° C., so that the actual amount in the austenite would almost certainly be not more than 0·30%; consequently the pearlite formed under a fairly rapid rate of cooling resembled that obtained in a low-manganese steel. For example, when a specimen of sample No. 1 and another of a steel containing carbon 0·10%, manganese 0·31%, sulphur 0·04%, and phosphorus 0·02%, were cooled together from 1,000° C. at a rate of 10° C. per min. through the critical range, the extent of the marginal coalescence in the two was about equal. Hence it was considered that this effect might be used as an indicator of the rate at which manganese diffused at different temperatures, and, in order to produce a gradient for the purpose, a welded sample was prepared as described below.

A 1¼-in. length was taken from a 1-in. diameter steel bar containing manganese 1·31%, carbon 0·12%, silicon 0·20%, sulphur 0·04%, and phosphorus 0·026%, and the centre was hollowed to within ¼ in. of the bottom with a ⅜-in. drill. The cavity was then nearly filled by inserting a ⅜-in. diameter rod of sample No. 3 and, after a short steel plug had been hammered in, the end was made completely gas-tight with a thick covering of arc-deposited metal. Finally, to weld the two steels together, the cylinder was heated to about 1,050° C., placed lengthwise on the anvil and forged down to a flat ¼-in. thick. A thorough weld was, of course, an essential requirement for diffusion, and, in order to ensure that this had been obtained, three sections from different parts were examined before proceeding with the tests. The positions of the weld were readily seen, for on the core side the pearlite areas were largely divorced, while on the other side they were entirely sorbitic. The junctions appeared to be clean and perfectly sound, since crystallisation had everywhere taken place across them. This having been ascertained, a test for diffusion was made by heating one of the sections together with a piece of sample No. 3 for 5 hours at 1,120° C., after which they were cooled through the critical range at a rate of 10° C. per min. The structures of the pearlite areas in the two specimens were then compared, but no indication that manganese had passed into the core could be seen, notwithstanding the steep gradient across the weld. Even at places adjacent to the junctions, the pearlite had coalesced to the same extent as that in the original sample. Seemingly, therefore, little if any diffusion of manganese into the core had occurred, an inference which was subsequently verified by a determination of the manganese content, for after very carefully filing away the easily visible outer steel, an increase of only 0·03% was found.

Having obtained so small a result a second test was made, this time at about 1,250° C., at which temperature a section of the welded piece was held for 3 hours; it was then withdrawn, reheated to 1,000° C. and cooled at the same rate as that employed in the previous test. Yet, even after this treatment, no diminution of the pearlite coalescence in the core could be detected, so that there was still no sign of any appreciable manganese diffusion. Thus the evidence indicated, at most, a very slow rate of manganese diffusion, so slow in fact that it was thought desirable to check this conclusion by means of an alternative method in which the conversion of FeS to MnS in solid steel was used as the indicator. This was, of course, a more direct attack on the problem under consideration—namely, the persistence of FeS in the segregate, and therefore no inference on diffusion could be drawn unless the above change occurred.

The occurrence of FeS in the segregate was of additional interest as being a direct and reliable indication of its presence in large amounts near the solidus point in this class of steel, and since this compound is known to cause redshortness, severe cracking of the ingots might be expected. In America especially, the opinion is now freely expressed that the hot-working quality of steel deteriorates as the sulphur content rises. McCance[1] also maintains that sulphur is a fundamental cause of cracking and supports this view with statistical data which show that, as the sulphur content increases from 0·025% to 0·05% the percentage of cracked ingots is more than doubled. He further states that the cracks appear within a few minutes of filling the mould or not at all. Yet very little trouble of that kind is experienced either in casting or in rolling the very highsulphur ingots of the type under discussion. The reason is by no means obvious, but, from the effects observed in the specimens, which were heated to within the liquidussolidus range, a tentative explanation may be suggested. To make this clear, however, it will be as well first to consider how the cracking of ingots may be affected by the casting conditions, and in so doing use will be made of the following two published observations:—

(1) Hultgren[2] some years ago demonstrated clearly that after-pouring disturbed the columnar crystallisation in ingots to within a short distance of the base, from which the reasonable inference may be drawn that, in top-filling, the stream from the nozzle can penetrate far down into the mould, even when it is almost full.

(2) Hall[3] has recently shown that, at temperatures just below the solidus, steels of different compositions are not only very weak, but have little or no elongation. Hence, when the ingot begins to solidify, the contraction stresses acting against the ferrostatic pressure may easily cause the early rupture noted by McCance. Of course, if a break occurs at the very outset of freezing, liquid metal may flow outwards and the rupture will be healed, but if it starts a little later, when a somewhat thicker skin has formed, the liquid within may not be reached and the crack will consequently tend to deepen as cooling proceeds.

Now, since in direct-teeming the stream seems to penetrate to a point near the bottom of the mould, it is to be expected that the whole of the metal, except perhaps that at the base, will remain molten, especially if very hot, until teeming is finished. Thus, freezing will commence almost simultaneously at all parts of the surface adjacent to the mould walls, with the result that contraction stresses, and therefore the tendency to cracking, will be at a maximum. When, on the other hand, the skin forms gradually from the base upwards, so that a distinct taper is produced, not only will the extent and suddenness of the overall contraction stresses be lessened, but also the lower part of the shell, being a little thicker and stronger, will be better able to withstand them. Incidentally, it may here be remarked that this condition is presumably brought about

1 McCance : "Symposium on Steelmaking." *Iron and Steel Institute*, 1938, *Special Report No.* 22, p. 331.
2 Hultgren : *Journal of the Iron and Steel Institute*, 1929, No. II, p. 69.
3 Hall : Second Report of the Steel Castings Research Committee, Section IV., *Iron and Steel Institute*, 1936, *Special Report No.* 15 ; Third Report of the Steel Castings Research Committee, Section IV., *Iron and Steel Institute*, 1938, *Special Report, No.* 23.

in the up-running method of casting, for, since the liquid steel then flows up the centre of the mould, the metal near the walls should be left relatively undisturbed. Consequently, freezing is more likely to begin in the lower half of the ingot first and even before the top half of the mould is filled. Much the same effect should occur also in tundishing, owing to the greatly reduced head of metal. The fact that both these methods of casting minimise cracking may thus be explained.

The above remarks are intended to relate chiefly to killed mild-to-medium carbon steel ingots of less than 15 tons in weight, for, given a sound skin about ¼ in. deep, subcutaneous blow-holes formed in unkilled steel tend to modify the contraction strains, apparently by acting as cushions. Now, as the liquidus-solidus range is widened, a similar effect seems to arise from the longer presence in the skin of liquid layers normal to the surface. At any rate, it is the author's experience that as the carbon content is raised above about 0·30%, the liability of direct-teemed solid ingots to cracking tends to diminish. In any one size of mould the change from the liquid to the completely solid state then takes place over a progressively lengthening period, with the result that the initial contraction compresses inwards the residual mother-liquor still between the crystallites and a rupture may thereby be avoided.

Having dealt with the sulphides, attention is given to the second type of inclusion found in the samples. As already stated, this consisted of globules, complex in structure, sometimes very large and by far the most numerous in sample No. 2. Their ground-mass was composed of a brittle, dark, translucent mixture of fine texture in which several very obvious rounded, opaque, dove-grey inclusions were usually embedded. From two to at least five types of

inclusion were observed in these complex globules, and for further reference it will be convenient to number them as follows :—

1. Large and also very small MnS inclusions.
2. A dark glassy substance in the ground-mass itself.
3. Extremely fine particles with a yellowish tint distributed in the ground-mass as a network or in lines.
4. Very dark idiomorphic crystals.
5. An opaque material resembling MnS in colour, but distinctly darker.

As already stated, the No. 1 class was undoubtedly MnS. The others had still to be identified, and, taking into account the fact that no deoxidisers except ferro-manganese were used in making the steel and also that it contained on the average at least 0·03% of oxygen, the following tentative conclusions were reached as a result of the careful inspection of the globules. Type No. 2 was in all probability a silicate. The yellowish tint which the extremely finely divided No. 3 gave to the ground-mass suggested FeS. Type No. 4 strongly resembled chromite both in colour and in shape, while No. 5, from its appearance, was judged to be FeO. Having formed these opinions, an endeavour was then made to verify them by means of the tests, the results of which are discussed. The evidence obtained from these tests indicated that the ground-mass was eutectiferous and belonged to the system MnS–FeS–fayalite–rhodonite with the occasional addition of FeO. In further support of this conclusion one other observation should be mentioned. As a rule, the larger inclusions within the globules were MnS, with sometimes FeO and/or the No. 4 type of inclusion, but once or twice a glassy silicate was found.

Influence of the Molybdenum Content upon the Properties of High-Speed Tungsten-Free Tool Steel

By D. W. Rudorff, A.Am.I.E.E., F.R.S.A., M.Inst.F.

The importance of molybdenum additions to high-speed tool steel is generally recognised, but a recent investigation on the influence of molybdenum on tungsten-free high-speed steel is of particular interest. Four steels, with varying molybdenum contents, were investigated and forged samples subjected to micro-analysis hardening tests, dilatometric, magnetometric, and cutting tests, and the results are given in this article.

IN view of the importance of molybdenum as alloying element in high-speed tool steel, a recent investigation[*] into the influence of the magnitude of the molybdenum content upon the characteristics of a tungsten-free high-speed tool steel is of particular interest. As Table I shows, the vanadium, chromium and carbon content of the four steels investigated is identical, while the respective molybdenum percentages are 0, 1·2, 2·3, and 3·2.

TABLE I.

Designation of Steel.	Carbon, %.	Vanadium, %.	Molybdenum, %.	Chromium, %.
0	1·3	4·2	—	4·3
01	1·3	4·2	1·2	4·2
02	1·2	4·2	2·3	4·3
03	1·3	4·2	3·2	4·3

The choice of these molybdenum percentages was based on preceding investigations in which a 3% molybdenum steel had been found to show excellent high-speed cutting properties ; and it was therefore decided to ascertain whether, and to which extent, this molybdenum content can be decreased without impairing the qualities of the steel.

* Professor A. Gulyaev: "Molybdenum in Low Alloyed High-speed Steels." *Stal*, No. 9, 1940, p. 33 et seq. (in Russian).

The samples subjected to test were 15 × 15 × 8 mm· thick. All pieces were found to forge well, although there was of course a noticeable decrease in the plasticity with increasing molybdenum content. The forged sample pieces were subjected to micro-analysis, hardening tests, dilatometric, magnetometric, and cutting tests.

Isothermal Decomposition of the Austenite in The Upper Range.

The first characteristic investigated was the isothermal decomposition of the austenite in the zone of pearlitic transformation. This investigation was made in accordance with the testing methods laid down by Davenport and Bain. The test results were used for the charting of S-curves (isothermal-reaction rate curves) for the various steels, showing the time for initiation of austenite decomposition after heating to a hardening temperature of 1,280° C. Referring to the graph reproduced in Fig. 1, it is seen that with the steels investigated, an addition of 1% molybdenum (steel " 01 ") considerably increases the austenite stability as compared to the molybdenum-free steel " 0 " ; while the addition of 2·3 or 3·2% molybdenum adds very little

to the improved stability of steel " 01." The critical cooling speeds found for the four steels range as follows :—

Steel " 0 " .... 28° C. per min.
   " 01 " .... 6° C.   "
   " 02 " .... 3·5° C. "
   " 03 " .... 3·0° C. "

This result shows that very little decrease in critical cooling speed is obtained by molybdenum contents above 1·0%.

Isothermal Transformation in the Second Zone

The magnetometric curves of the isothermal transformation in the second zone (200°–400° C.) for the steels " O," " 01," and " 03 " are charted in Figs. 2, 3, and 4 respectively. The most intense transformation is seen to take place at 300° C. in the graph shown in Fig. 4. Transformation at this temperature, and also at 250°, effects a depression of the martensitic point of the residual austenite below 0° C. The test run at 400° C. is seen to be unaccompanied by austenitic decomposition, and without exercising any influence upon the position of the martensitic point. Heat-treatment at less than 400° C., as, for instance, at 350° C., shows likewise no austenitic decomposition in the case of steel " 03 " (Fig. 4); it leads, however, to a considerable depression of the martensitic point and to an increase in the quantity of residual austenite. The same can be said of the tests conducted with all three molybdenum steels at 190°–200° C.

The diagrams given in Figs. 2, 3, and 4 show that isothermal treatment in the intermediate range leads to a depression of the martensitic point and to an increase in residual austenite, irrespective of whether or not the heat-treatment leads to austenitic transformation. From these graphs an influence of the molybdenum content upon the transformation of austenite in the second zone cannot be deduced.
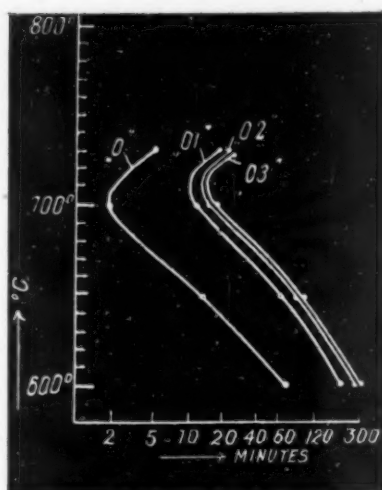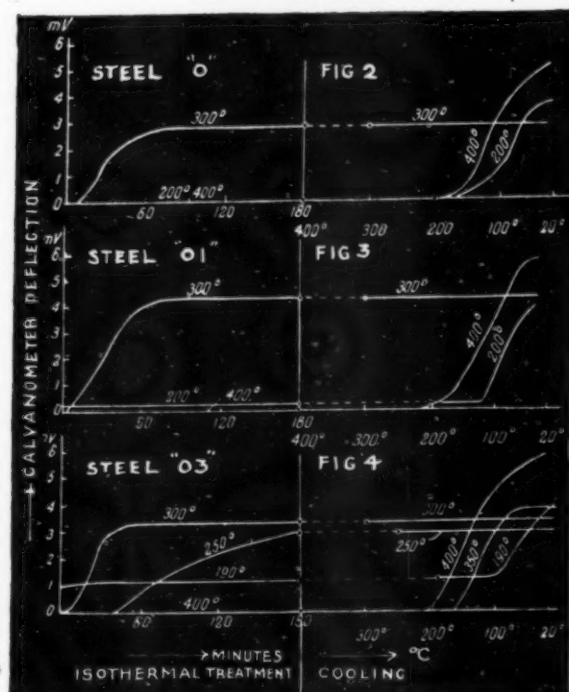

Fig. 1.—Time required for the initiation of austenite decomposition at various temperatures after heating to hardening temperature of 1,280° C.
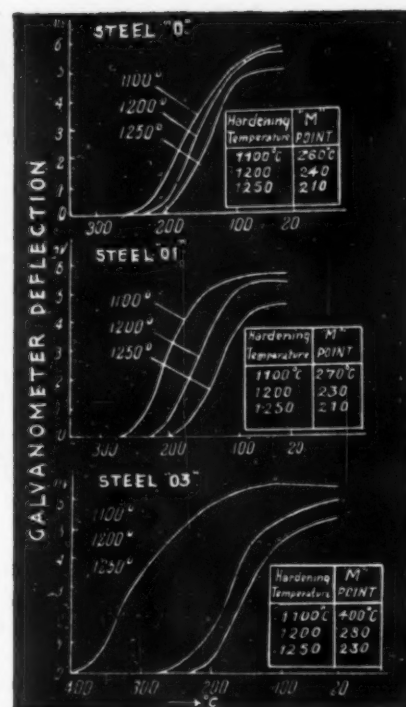

Figs. 2, 3 and 4.—Isothermal decomposition of austenite in the second zone.

Fig. 5.—The martensitic points as function of the quenching temperature in steels " 0," " 01," and " 03."

Martensitic Transformation

In Fig. 5 are charted the magnetometric curves obtained with the steels " 0," " 01," and " 03 " which curves serve to determine the martensitic point as function of the quenching temperature. These curves show that like ordinary high-speed tool steels, the three steels develop a depression of the martensitic point with increased hardening temperature. It is also seen that increased molybdenum content tends to raise the martensitic point in the case of constant quenching temperature ; thus, for instance, with steel " 03," containing 3·2% molybdenum, point M lies at 280° C. when the steel is quenched from 1,200 C., as compared to a martensitic point of 230° C. in the case of steel " 01," with 1·2% molybdenum quenched from the same temperature.

Determination of the amount of residual austenite after hardening shows (Fig. 6) that increased quenching temperature leads to increased residual austenite content. For identical temperatures of hardening, steels with larger molybdenum content exhibit, as a rule, smaller residual austenite content in the hardened as well as in the tempered state.

The Influence of the Hardening Temperature

With a decrease in hardening temperature, the four steels investigated behave in a very similar manner ; leaving aside, of course, the specific effects of their respective molybdenum contents. In the case of quenching from 1,000° C., the structure of all four steels was found to consist of primary martensite, their hardness being somewhat below 60 Rockwell C (Fig. 7). With a hardening temperature of 1,100° C., the primary hardness of the steels is seen to reach its maximum value of 64–65 Rockwell C., and it does not exhibit any pronounced tendency towards falling off when higher hardening temperatures up to 1,300° C. are employed, and this in spite of the somewhat increased amount of residual austenite. Molybdenum is known to decrease the grain size of the austenite, therefore the greater the molybdenum content of the steel, the more refined is the structure of the austenite for one and the same hardening temperature.

The Influence of the Drawing Temperature

The influence exerted by the drawing temperature upon the hardness is evidenced by the graphs charted in Fig. 7. In this test, the test-pieces were quenched from 1,000°,
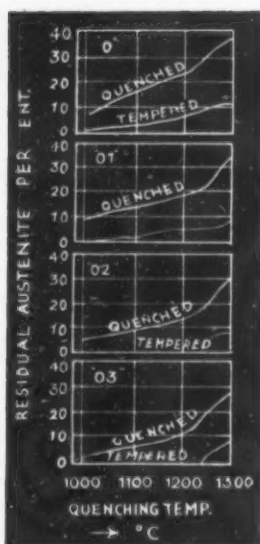
Fig. 6.—Residual austenite content of steels "0," "01," "02," and "03," as function of the hardening temperature.

Fig. 7.—Influence of the penetration of draw upon the hardness of steels "0," "01," "02," and "03," hardened from 1,300°, 1,240°, 1,100° and 1,000° C.

1,100°, 1,240°, or 1,300° C., and then tempered at various temperatures ranging from 100° to 650° C. The curves charted show the characteristic decrease in hardness with the average drawing temperature of 300°–400° C., while secondary hardening is exhibited with tempering at 500°–600° C. A comparative study of the charts obtained with the four different steels, leads to several conclusions, to wit :—In the case of the steels with no or only small molybdenum content, the decrease in hardness with the drawing temperature is large because of the large quantity of austenite in these steels, but for the same reason, their secondary hardness is somewhat more pronounced. As Fig. 6 shows, one-hour tempering at 560° C. leads to a sufficiently complete decomposition of the residual austenite.

TABLE II.
INFLUENCE OF 1-HOUR TEMPERING AT VARIOUS TEMPERATURES UPON THE ELEVATION OF POINT M_1.

Temperature of Draw, ° C.	Steel.		
	" 0."	" 01."	" 03."
300	280°	280°	—
560	360°	370°	300°
600	420°	400°	350°

TABLE III.
INFLUENCE OF THE LENGTH OF TIME OF TEMPERING AT 560° C. UPON THE ELEVATION OF POINT M_1.

Length of Time.	Steel.		
	" 0."	" 01."	" 03."
10 mins.	360°	335°	290°
1 hour	360°	370°	300°
3 hours	410°	380°	340°

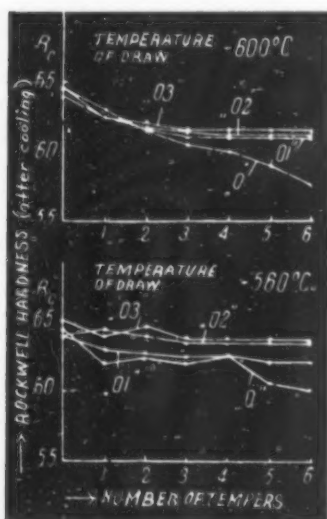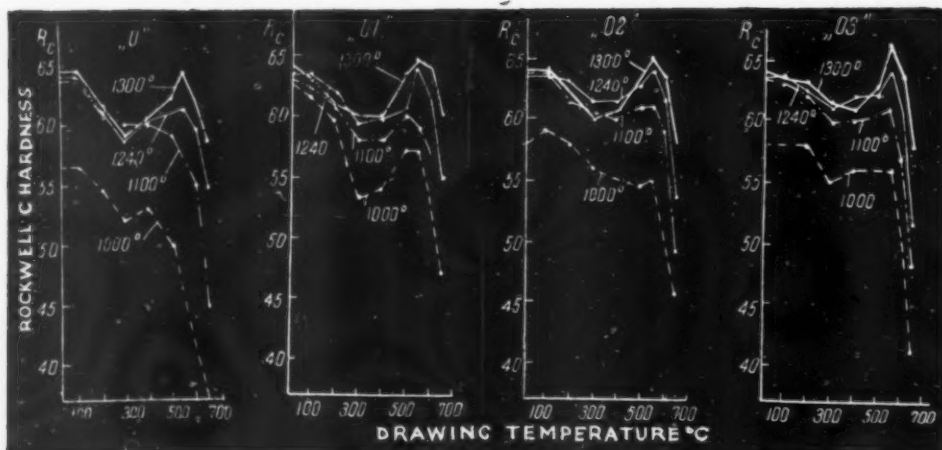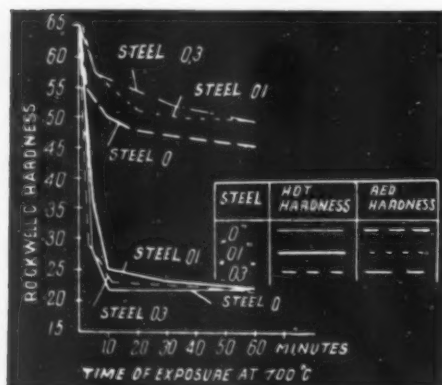The effect of the drawing temperature (with 1-hour tempering) upon the elevation of the temperature of

Fig. 8.—Softening resistance (red hardness) of steels "0," "01," "02," and "03."

Fig. 9.—Hot hardness at 700° C. and resistance to softening (red hardness) at 700° C., as functions of time of exposure.

secondary martensitic transformation in the steels "0," "01," and "03," is shown in the subjoined Table II, while the influence of the length of treatment at the drawing temperature of 560° C. is tabulated in Table III.

From these data the following deductions are made by the investigator : Increased temperature of length of drawing increases the temperature of the secondary martensitic transformation. For a given temperature or length of draw, the temperature of secondary martensitic transformation decreases with increasing molybdenum content. Isothermal transformation at the temperature of draw proceeds more slowly with steel "01" than with steel "0" and still more slowly (only after 3 hours of tempering) with steel "03." Molybdenum, therefore, is seen to delay the transformation and to render austenite more stable against transformation at the tempering temperature. The investigation also confirmed the tendency of molybdenum to increase the depth of decarburisation. It is of interest to note that the initial addition of 1% molybdenum almost doubled the decarburisation, while further increases in the molybdenum content caused relatively much smaller increases.

Resistance to Softening

A special series of tests was run with a view to ascertaining the red-hardness of the various steels—that is, their ability to retain initial hardness up to red heat and to remain unaffected after cooling. For this purpose, test-pieces quenched from various temperatures (1,200°, 1,270°, and 1,300° C.) and tempered at 560° C., were subjected to repeated heating to 560° and 600° C. respectively. The results of the test run with the pieces hardened from 1,300° C. are charted in Fig. 8, where it is seen that at 560° C. all steels investigated showed good red-hardness, although the molybdenum-free steel "0" showed as tendency to softening after the fourth tempering cycle. This tendency of the molybdenum-free steel became still more pronounced in the test run at 600° C.

Parallel with these tests, another series of tests was made in which the hot hardness—that is, the actual hardness of the steel at the elevated temperature—was ascertained. For this purpose, specimens of the various steels, quenched from 1,270° C. and drawn at 560° C., were heated to 700° C. and tested at this temperature in a hardness tester
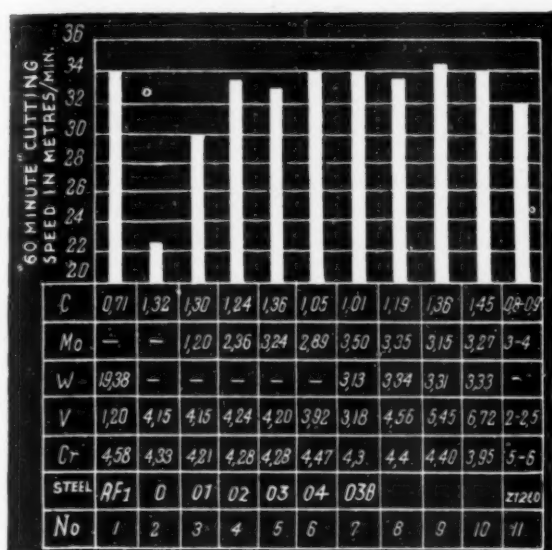
Fig. 10.—" Sixty-minutes " cutting speeds.

Fig. 11.—Molybdenum high-speed tool steel characteristics versus molybdenum content (other alloying constituents) 1.3% C, 4% V, 4% Cr.

of the impact type. After cooling, the hardness was again measured. The findings (converted into Rockwell units) are charted in Fig. 9, which shows the relationship between the hardness of the test-piece in hot versus cold state as influenced by the length of heat-treatment at 700° C. The diagram shows that at 700° C. the hot-hardness of the three steels is practically identical, and this irrespective of the length of heat-treatment. The red-hardness (measured in cold state) of the various steels, however, is seen to differ considerably, the molybdenum-free steel " 0 " showing definitely inferior red-hardness to both " 01 " and " 03 " steel. After about 10 mins. exposure, the superiority of steel " 03 " over " 01 " becomes very marked, and only after 60 mins. exposure has the red-hardness of steel " 03 " decreased to that of steel " 01."

The superiority of steel " 03 " is amply confirmed by actual cutting tests, and it is therefore only too clear that the hot-hardness test cannot be accepted as criterion of the cutting qualities.

Tool Life Investigations

The cutting tests were made with a hard carbon steel of 220–230 Brinell, containing 0·58% C, 0·69% Mn, 0·24% Si, 0·016% S, 0·21% P, 0·33% Ni, and 0·16% Cr. The tests were conducted without the use of a cutting fluid, with the chip section held at $3 \times 0 \cdot 31$ mm. The cutting tools made of the various steels under investigation were oil-quenched from 1,280° C. and triplex tempered at 560° C. In order to be able to judge the steels " 01," " 02 " and " 03 " on a broader basis, it was decided to include the high tungsten steel RF1 and the tool steel Z.I. 260 in the test. The percentages of the major alloying elements of these two steels are given in Fig. 10. Steel RF1 was quenched from 1,300° C., and triplex drawn at 560° C., and steel Z.I. 260 was quenched from 1,300° C. and duplex tempered at 560° C. Furthermore, two modifications of steel " 03 " were prepared, the one of them (designated " 04 ") containing less carbon than steel " 03," while the other modification (designated " 03 в ") received an addition of 3% tungsten.

For the cutting tools, the characteristic cutting curves were established according to $T = f(v)$, hereby obtaining the specific cutting speed at which the tool life amounts to 1 hour. The latter speeds are charted in Fig. 10. From these data it can be concluded (1) that a molybdenum percentage of 2–2·5 added to a 4% V, 4% Cr steel increases the cutti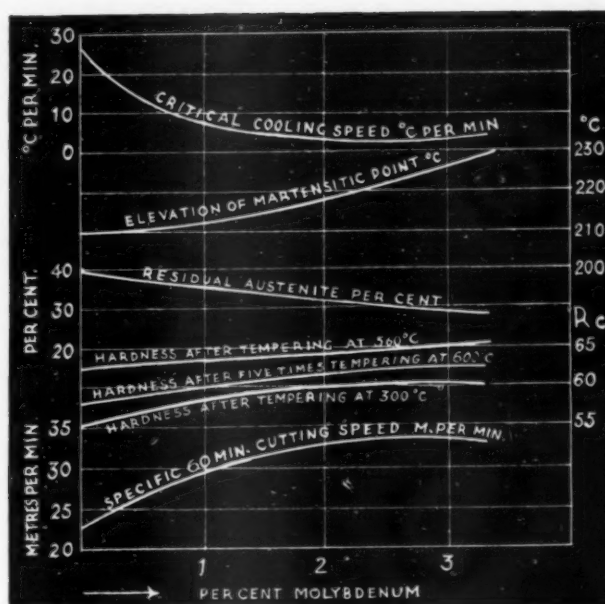ng properties ; while higher molybdenum contents are without influence in this respect. (see steels No. 2, 3, 4 versus No. 5) ; (2) the initial carbon content of 1·3% can be lowered to about 1·05% without diminishing the cutting properties. (see steels No. 4 and 5 versus No. 6) ; (3) the addition of 3% tungsten causes only an insignificant improvement in cutting qualities (see steel No. 5 versus steel No. 8). The influence of the magnitude of the molybdenum content upon the properties of the steel investigated (containing 1·3% C, 4% V, an 4% Cr) is particularly well illustrated by the composite diagrams Fig. 11, showing the various findings as direct function of the molybdenum content. Finally, it may be mentioned that on the basis of these findings the following composition is recommended :—1·1–1·22% C, 2·4–2·9% Mo, 2·8–3·3% V, 3·8–4·6% Cr.

Orsk Metallurgical Combine

WORK is in progress on the building of the Orsk Metallurgical Combine, about eleven miles from Orsk, in the Urals. The first section will comprise two blast furnaces, two coke batteries, part of a steel furnace plant, and the corresponding ore mining plant. This section is scheduled for operation in 1943, and the whole of the combine is to be completed by 1945.

The reserves of ore and limestone at the Akkerman and Nono-Kiev iron ore deposits are being explored with a view to forming a reliable estimate of the ore available in these areas. Prospecting of the manganese ores in the Khalilov district is now completed, and plant is being erected to deal with the ore deposits of Novo-Kiev, as well as a crushing plant at the Akkerman deposit. To maintain a regular supply of water to meet the requirements of the combine, a reservoir is in progress of construction at Iriklin, 50 miles from Orsk.

When completed the Orsk Metallurgical Combine will have four large blast furnaces capable of producing in the aggregate 1,200,000 tons of pig iron a year. The projected capacity of the open-hearth furnaces and the rolling mill plant is one million tons of steel and 800,000 tons of rolled metal. The plant will include coke and by-product plant, and the necessary auxiliary and subsidiary plant and equipment for a self-contained works of this nature.

Electrolytic Polishing of Steel Specimens

An electrolytic method of polishing is described which, used on specimens of low-carbon or low-alloy steels, gives results comparable with those obtained by competent mechanical polishing, while ferrite and austenite stainless alloys can be polished by the method to a degree difficult to attain mechanically.

POLISHING steel specimens for microscopic examination is always difficult, and polishing must be of a high order to assure efficient examination. The mechanical method of polishing is the one most generally used, but during recent years a method of polishing of an electrolytic type has been originated by Jacquet and Rocquet. An electrolytic method of polishing and how to use it has recently been described by G. F. Meyer, G. D. Rahrer and J. R. Vilella*, and the results obtained by this method have been compared with those obtained by a mechanical polishing method. As a result it is stated that specimens of low-carbon or low-alloy steels can be polished electrolytically with a degree of perfection comparable to that obtained by competent mechanical polishing, and that ferrite and austenite stainless alloys can be polished electrolytically with a degree of perfection difficult to attain mechanically.

The electrolyte for polishing plain carbon and alloy steels consists of 185 cc. of perchloric acid (spec. grav. 1·61) in a vessel placed inside a larger receptacle containing ice or through which cold water is circulated. To the perchloric acid 765 cc. of pure acetic anhydride is gradually added then 50 cc. of distilled water, and the solution is allowed to remain at ordinary temperature for 24 hours before using. The solution for polishing stainless steel is prepared similarly but contains 335 cc. perchloric acid, 665 cc. of acetic anhydride and no water. Neither electrolyte deteriorates on standing, but both lose potency with use, but their original efficiency can be restored by the addition of 1 per cent. by volume of water. Dissolving 0·5 per cent. of aluminium by anodic attack in the solution for plain carbon steels increases the viscosity of the electrolyte, permitting more vigorous agitation and the use of a smaller current density.

The specimen to be polished constitutes the anode of the cell and should be free from all trace of grease or oil Any scale present should be ground off before it is placed in the electrolyte. The cathode can be either a sheet of aluminium, carbon steel or stainless steel, and no effect on the quality of the final polish of the specimen was observed when the area of the cathode was varied between 10 and 30 times that of the specimen. The position of the cathode with respect to the specimen, whether above, below or to one side, did not influence the final result, although a distance of ¾ to 1 in. between specimen and cathode was found satisfactory.

Proper adjustment of the current density is the factor which, more than any other, affects the quality of the result. For plain carbon and low-alloy steels a current density of 5 amp. per sq. decimeter of total anode surface (0·3 amp. per sq. in.) is best. If the current density is too low the specimen is likely to be etched deeply and the grinding scratches not removed, while if too high pitting may occur. For stainless steel a minimum current density of 7 amp. per sq. decimeter (0·45 amp. per sq. in.) should be used. Stainless steels do not require the same careful regulation of current as do plain carbon steels, but nothing is gained by using a higher current density. The required current for a given specimen is based upon the total immersed area, and in the case of a group of thin sheets assembled as a single specimen in a clamp, the total increased area comprises both the full immersed area of

each sheet (both sides) and the area of the clamp in addition.

With the proper current density, the time required for a satisfactory polish decreases with the fineness of the grinding scratches present on the specimen. In plain carbon and low-alloy steels the scratches produced by 500 mesh grit 000 emery paper can be removed in approximately five minutes. Stainless steels similarly ground can be electro-polished free from scratches in four minutes, but an attack of this duration is seldom sufficient to remove all traces of disturbed metal. The waviness of the finished surface, which is frequently observed in electro-polished specimens can be minimised greatly by agitating the solution by stirring or by bubbling air through it. Minimum waviness occurs when the stirring is rapid and causes irregular movement of the electrolyte in immediate contact with the specimen.

The sequence of steps in electro-polishing consists in first grinding off the scale and removing all traces of grease. The area is then measured and the current required to produce the required density calculated. The specimen is then connected to the positive wire and inserted in the electrolyte which must be agitated and not permitted to rise in temperature above 85° F. (30° C.) at any time. The current is then adjusted to the calculated density by means of a rheostat, and during the first 20 seconds tends to fall and the voltage to rise, this change coinciding with the formation of a reddish-brown deposit on the specimen. While this is taking place the current is adjusted to maintain the calculated density, after which it remains constant. When the attack is complete, the specimen is washed, dried and etched.

A variety of steels ranging in carbon content from a trace to 1·8 per cent., comprising practically all the microstructures common to those steels, together with a number of low alloy and stainless steels, were electro-polished satisfactorily. Their polished surfaces exhibited certain defects of which the most frequent were an undulating rather than a plane surface ; high relief of the carbide particles, particularly when they were coarse, as in spheroidized structures ; and attack on non-metallic inclusions. The waviness of surfaces and the relief effect of the carbide particles, if kept to a minimum, did not interfere seriously with the proper development of the structure by etching, or with its microscopic examination. Attack on the non-metallic inclusion was inclined to be excessive, particularly in low carbon steels, and made the metal appear considerably " dirtier " than it actually was. In this respect the electrolytic method yielded results inferior to good mechanical polishing.

Optimum results by the electrolytic method of polishing were obtained when the specimens were ground to the same fineness as for mechanical polishing. It was found that in general, the finer the grinding, the shorter the time required to produce a satisfactory polish, the less the waviness and relief effect, and the less the attack on the non-metallic inclusions. In mechanical polishing it is often necessary to repolish, re-etch and examine the structure microscopically several times in order to be sure that all traces of disturbed metal have been eliminated, but in electrolytic polishing it was often found possible to dissolve all the disturbed metal by a single treatment. The time generally required to polish electrolytically after the

Institute of British Foundrymen
Annual General Meeting at Manchester

Despite the difficulties associated with present war conditions, this meeting proved a substantial success, and some 200 members were present during the morning session, the majority of whom attended the luncheon. The technical papers presented, which are briefly referred to in this article, created much healthy discussion.

IN spite of the difficulties associated with the operation of the various British technical societies' activities during war time, these activities have been remarkably well maintained, and the Institute of British Foundrymen, which held its annual general meeting in Manchester on July 12, is no exception to this rule. True, there has been some curtailment of work and the duration of the annual meeting has been reduced to a single day, but the work of the various branches has been continued successfully throughout the year. Four of the branches carried out normal programmes of technical meetings and, with the exception of two, all the remaining branches organised some meetings for the presentation and discussion of papers.

In view of the difficulties encountered, this meeting was very successful, over 200 members attending the initial business meeting, at which the retiring president, Mr. W. B. Lake, J.P., presided. At the conclusion of the normal business, which included the announcement of awards, the election of officers and the result of the ballot for the election of five members of the Council, the president-elect, Major R. Miles, was duly installed.

Presidential Address

In his presidential address, Major Miles intended to give a general review of the development, present position and prospects of the foundry industry, but for obvious reasons the time was not opportune to disclose facts and figures of our industry so closely associated with the war effort. In the circumstances, therefore, he restricted his remarks to a few general observations connected with the war, and made a number of suggestions concerning post-war conditions. He was convinced that whatever set-backs the present war may produce, whatever discomfort or sorrow individuals may experience, the general progress of mankind will not be impeded, and the efforts of the industry to meet the needs of the community will in the long run be in no wise impeded.

In a world where abnormalities and aberrations exist, they must be dealt with whether they occur politically in a nation, or psychologically in any mass of people, in exactly the same way as they would be treated as a disease of the human body, or morbidity of an individual mind. When such nations as the Germans have learned to shed their barbarity, other methods of dealing with diseased mass psychology will be employed, but in the meantime the surgical operation necessary requires the implements of war. The immediate position of the foundry industry, therefore, is clear : to provide an ample supply of castings to this end. The future, however, is not so obvious.

When hostilities cease and, later, when the vast numbers of men and women engaged directly and indirectly for war purposes revert to peaceful pursuits, considerable forethought will be necessary to guide the change. The problem is of the same magnitude as the change from peace to war. The speed at which change can be effected will probably be no greater, and it is almost inevitable that " control " will persist for some years after the war has ended.

Control, in the case of the foundry, will need to be particularly widespread, as this industry rarely sells its products direct to the final consumer. For the most part, its products are raw materials to other industries, upon which there are numerous operations. Hence from the point of view of marketing, any national plan designed to serve foundry interests cannot be restricted to the foundry interests alone ; it will need to form part of a much wider plan.

Major Miles made some observations on the release of man-power by mechanised systems of production and their effect in reducing the working week still further within the present generation, and suggested the need for training to make proper use of increased leisure. The standard of education in this country and appreciation of the good things of life is certainly higher than in many other populous countries, but this high standard carries an obligation, and its maintenance demands vigorous and successful pursuit of scientific research and development. It is not sufficient to ensure that research is successful academically, but, by suitable propaganda and otherwise, to ensure that a practical realisation of exchangeable value accrues from the efforts made. In conclusion, the President said that the present duty of the Institute is to continue a leading part in helping to win the war and its future duty is to use, jointly and severally, its abilities to ensure that the industry maintains its part in serving mankind.

Probably the most important point stressed by the President was the need for an organised effort by the industry to place itself in a position to cope with difficult conditions that are bound to be experienced when hostilities cease. There is no doubt, as he suggests, that the Institute should give a lead in this matter, but it is really the individual member who should get busy and press the Council to appoint a special committee to weigh up suggestions and develop some scheme which could form the basis of a report to the Council. The foundry industry is sufficiently important to take the initiative in developing a workable scheme, and the sooner something is done about it the better will be the foundry's position to meet difficult times ahead.

Presentation of Awards

Oliver Stubbs Medal.—Mr. J. J. Sheenan, foundry manager, Austin Motor Co., was awarded the Oliver Stubbs Medal in recognition of his many papers to various branches of the Institute, exchange papers presented to overseas Institutes, and also at International Foundry Congresses. The award also is an acknowledgement of his valuable work as Convener of the Sands Sub-Committee of the Technical Committee.

E. J. Fox Gold Medal.—This medal was awarded to Mr. Percy Pritchard in recognition of the scientific and technical contributions which he has made to the development of the foundry industry, particularly in light aluminium and magnesium alloys. Mr. Pritchard is managing director of the Birmingham Aluminium Co., Ltd., the Midland Motor Cylinder Co., Ltd., and Birmid Industries, Ltd.

Meritorious Services Medal.—The Council of the Institute awarded the Meritorious Services Medal for 1941 to Mr. H. W. Lockwood, of the London Branch, in recognition of the valuable services which he rendered to the Institute in his capacity of honorary secretary of that Branch over a period of many years.

Diplomas.—The Council accepted the recommendations

of the Literary and Awards Committee, and diplomas have been awarded to the following authors of papers presented during the past session :—J. R. Webster, for his paper on " Rope Pulleys," presented before the Scottish Branch ; A. E. McRae Smith, for his paper on " Melting and Casting Problems in the Production of High-strength and Special Duty Iron Castings," presented before the Lancashire and London Branches ; and J. M. Stones, for his paper on " Some Notes on Bell Founding," presented before the South African Branch.

TECHNICAL SESSIONS

Owing to the meeting being limited to one day only four papers were presented, and for convenience two separate sessions were held simultaneously, at one of which was an American Foundrymen's Association exchange paper by Norman J. Dunbeck, entitled " American Synthetic Sand Practice " ; this paper was presented by J. J. Sheehan. The main features of the subjects discussed in the papers are given in the following notes :—

American Synthetic Sand Practice

A synthetic sand may be made from all new unbonded sand and clay ; from naturally bonded sand and clay ; from used moulding or core sand and clay or from combinations of these various materials. When it is proposed to rebond certain sand heaps it should be realised that there is a certain loss of sand on the castings of which only a portion is recovered. This loss must be replaced by daily additions of sand which may be any of the above materials. The original sand in the heap will eventually be entirely replaced by the sand in the daily addition resulting in a final mixture composed of the base material and bond. The final result is the same, therefore, whether a start is made with a completely new synthetic mix or whether rebonded old sand is the original material.

The base sand may be a bonded sand, a low-bonded sand or an unbonded sand. An unbonded sand is preferable since the clay in naturally bonded sands is neither usually efficient nor refractory. The so-called bond in natural sands also frequently contains a substantial percentage of silt which adds little to strength, increases the amount of tempering water required, and reduces permeability and flowability. Some low-bonded sands are desirable since the small amount of natural clay present provides a priming surface on the grains and substantially reduces the amount of bonding clay which must be added. Any final decision on base sand depends upon the delivered cost, a cheap local low-bonded sand being preferable to a costly distant unbonded sand.

The base sand is examined for these four properties : (1) Grain size, shape and distribution ; (2) minimum clay content ; (3) refractory value ; and (4) minimum expansion.

The reasons for stipulating minimum clay content, minimum expansion and maximum refractory value are apparent. Some thought must be given to grain size, shape and distribution. While the type of bond clay used will have effect upon flowability and hence finish, it is true that fine finish is obtained only from fine-grained sands. While the type of clay will affect the permeability, it is still true that very high permeabilities are given only by comparatively coarse sands. One must, therefore, seek the proper grain-size for the work to be done. In the search for such sand grain shape and distribution must also receive attention.

In any moulding sand, foundrymen are interested principally in grain-size, green strength, dry strength, hot strength, permeability, durability, flowability, moisture required, resilience, expansion, contraction and sintering point. In selecting a naturally bonded sand, there is the difficult problem of finding as many of these twelve properties as well developed as possible within an economical radius of location. In compounding a synthetic sand, only three properties must be found—grain size, permeability, and expansion—as they are to be established in the base

sands, and foundrymen can control the other nine properties to a substantial extent by their selection of clay bond to be used. Since there are many types of clay available, the problem of making a synthetic sand is considerably simpler than the problem of finding an equally satisfactory naturally bonded sand.

Almost any kind of plastic clay will develop some binding strength. Special clays are used, because the clay should not only give green strength, but must also develop dry strength ; have a high sintering point ; the ability to mix rapidly ; good durability ; adequate strength at high temperatures ; moderate contraction at high temperatures, and other special requirements for specific problems. Their selection requires a knowledge of the essential properties of the general group of clays. Mr. Dunbeck discusses at length the properties of three main kinds of clays, known as kaolinite, illite, and montmorillonite clays, from which a choice can be made to suit the particular class of work to be done.

Considerable attention is given to the methods adopted for adding bonding clays to moulding sand in the foundry, in mixing mills, in sand-handling systems, and in facing sands ; reference is also made to its application in sand reclamation. In any application of clay bond, however, it is important to mix the bond and sand dry before adding tempering water. This results in much higher efficiency from the clay, and eliminates the possibility of clay balls being formed by the addition of water to the bond before it has been distributed through the sand.

There is also a growing tendency to keep some bonding clay available in all foundries even though naturally bonded sand is the principal material used. The bond is used to bolster up weak natural sands ; to add strength to facing sands, and to build up heaps which ordinarily require excessive additions of new sand. Such a heap would be one in which large quantities of burned core sand fell into the heap upon shaking out castings or where very heavy castings burned the sand badly on each pouring. The addition of the necessary amount of new sand to restore strength would result in a large surplus, and the daily discarding of enough old sand to make room for the new material. In such cases, clay bond is used in place of new sand, or in addition to the use of a reduced quantity of new sand.

In testing comparative value of clays the following conditions are necessary for accurate results :—

(1) All materials must be carefully measured or weighed.
 (a) The difference caused by careless measuring of several scoops of clay may be greater than the actual difference in strength of materials being compared.
 (b) Different clays vary considerably in weight per unit.
(2) All materials must be entirely dry.
 (a) A difference of $\frac{1}{2}\%$ in water content in a damp silica sand cannot be detected by observation, but may account for as much as 18% difference in results.
 (b) A difference of a few per cent. in natural moisture content of a clay may cause up to 30% difference in strength. A fire clay may appear perfectly dry when containing 4% water and a bentonite may appear dry when containing 10% water.
 (c) The moisture content of clay affects strength not only through its replacement of equal quantity of bonding material, but most importantly by its reduction of rate of distribution of the clay.

(3) Clays of the same type should be tested at exactly the same moisture content in the sand. The stronger sand will feel drier and may be too dry for moulding. Proper procedure is then to keep moisture

the same and reduce amount of clay. Common and incorrect procedure is to add water until both batches have the same feel. Since synthetic mixes get weaker as they get wetter, such water addition destroys the difference in strength which it was intended to measure.

(4) Test specimens should be tested individually as produced to avoid the effect of rapid surface drying.

(5) Since variables are unavoidable in large-scale foundry tests, final report should average results from at least three batches or mixes

(6) A standard should be run with each test because of the effect of atmospheric conditions. This important precaution is rather universally disregarded.

The author comments on the disadvantages of naturally bonded sand and also on synthetic sands, but the advantages of the latter certainly seem to outweigh any possible disadvantages, and the author has no doubt about the matter, as will be seen from the following points he makes :

(1) Synthetic sands make possible substantial savings. The cost of hauling used sand to a mixer is no greater than the cost of hauling it to the dump. The cost of transporting rebonded sand to the point of use is no greater than the cost of taking in an equal quantity of new naturally bonded sand. The handling costs cancel out, therefore, and the charges against synthetic sand are the cost of the bond clay, the cost of any silica sand additions, and the cost of mixing.

(2) They have much greater durability or life than naturally bonded sands, and one ton of synthetic sand may maintain strength for 50 to 200% longer than a ton of naturally bonded sand.

(3) Silica sands are much more uniform than naturally bonded sands, and bonding clays are dependably uniform. Since the foundryman is making a definite mix to satisfy his own conditions from uniform materials, the result is a much better control over sand conditions.

(4) The base sand will be free of silt, and the bonding clay will be very low in silt. The fine material in the sand will be almost all active bonding clay. This results in higher permeability, better flowability, and considerably less tempering water required.

(5) Synthetic sands are almost always more refractory, and give higher sintering points than naturally bonded sands. This results in better stripping and lower cleaning costs.

(6) Being made from simple materials, synthetic sand is easy to control, and American practice shows a sharp reduction in scrap losses with a change to synthetic sand.

(7) Synthetic sand, being made as required, eliminates the investment in carrying a winter supply of natural sand in storage, and eliminates the difficulties due to such sand freezing in unheated bins.

Mould and Core Washes

The practice of mixing blackwash in the iron foundry was at one time carried out with great secrecy, and it is noteworthy that in present days W. Y. Buchanan can deal with the subject of mould and core washes so fully, in which he considers their preparation and possible methods of testing. In general, the castings produced in British foundries are outstanding in regard to finish, a result which is due largely to the character and quality of the washes applied to their moulds.

The materials used in manufacture of blacking have been listed at great length elsewhere, including many forms of carbon more or less rare, and for that reason expensive, but usually the base material is coke breeze and possibly some additions of fireclay.

Where fireclay is added, it is usually the custom, especially when subsequently mixed by hand, to make no further additions except water in the making of blackwash. The author has for a number of years used blacking made from coke only and added to the resultant blackwash such materials as bentonite, Colbond, dextrine, semi-solid core oil, coal dust of high volatile content, and even crude oil.

The object of the bentonite, Colbond, dextrine and core oil was to prevent the blacking rubbing away readily after drying, although the core oil acts in a manner different from the clays. The coal dust was used with the same object in view, it being intended that at the drying temperature the volatile matter would be driven off and during the process a slight coking or crusting would take place.

Special additions such as alkalis, intended to improve the suspension of the clays in water, were not used owing to their corrosive action on the mixing tank, but crude oil was tried because of its action on coke dust, as in the Froth flotation process. The application of this crude oil is only possible when an emulsifier is used in the mixing process, such as is described later in the Paper.

Coke has a specific gravity of about 1·3—i.e., very near to that of water—is by nature very hard and abrasive towards metals even when finely ground, has a low percentage of volatile matter, high-fixed carbon, and usually low ash. Blackwash consists essentially of blacking and water plus additions, varying in concentration from a thin liquid to, in some cases, a heavy mud.

Mr. Buchanan gives considerable attention to the method of mixing the blackwash, and discusses facilities for mechanical mixing. Particular reference is made to a mixer operated by compressed air, a system which is now in continuous operation. The usual practice is to mix a new batch of blackwash and leave it overnight while the previous batch is still in use, so that there is no break in the continuous supply. A typical mixture in use at present is—

Blacking	224 lb.
Plumbago	12 lb.
Bentonite	20 lb.
Water	500 lb.

Defects in mould surfaces often throw suspicion on the blackwash used, and previously the blackwash mixture would be blamed or exonerated equally without evidence of any reliable kind being available, and this lack of any test-method usually kept the foundryman using a certain brand of blacking exclusively, irrespective of price and afraid to make any change.

The use of controlled mechanical mixing methods made it easy to reproduce the exact conditions each time, and so blackings could be prepared and compared on exactly the same footing. To maintain uniformity, however, the author considers it desirable to carry out routine tests and several methods are discussed.

Moulding Steam Valve Lids for Marine Service

For many years, cast non-ferrous alloys have been widely used on board ship for lids in boiler stop and manœuvring valves. The lid, in a marine valve, is that disc-shaped casting attached to the operating spindle which forms the valve component controlling the flow of steam between boiler and turbine. For this important duty it is obvious that the alloy employed should possess certain properties at elevated temperatures in order to withstand the effects of superheated steam, and castings made from it must be perfectly sound in every way. The necessary service conditions are being met by the use of nickel alloys of one kind or another, the melting of which is not unduly difficult, providing a good furnace is available and full use made of correct melting technique, embodying those principles which have received considerable mention in technical literature during the past few years—namely, the need of an oxidation followed by adequate deoxidation treatment. The supply of good metal, however, constitutes only one problem out of many in the production of sound castings and no one will deny that moulding methods introduce a problem of equal, if not greater, importance in obtaining practical results. This is particularly true in connection with the type of casting discussed by F. Hudson in this paper, as not only is very little published information available on moulding methods, but the need of such is emphasised by the variety of awkward designs in service. Consideration of moulding methods known to give good

results will obviously, therefore, be of considerable value to many non-ferrous founders at the present time in facilitating production of a type of casting playing an active part in the national effort.

Pouring temperature for all the nickel alloys used for valve lids is high, being between 1,450° and 1,550° C. according to the composition employed. Unlike gunmetal, however, there is a wide latitude in this direction, and the relation between pouring temperature and casting section is not critical. Every endeavour should be made to pour as hot as possible. The temperature range required is outside the scope of the most suitable foundry type of immersion pyrometer, but a very good guide can be obtained by testing the metal with a ¼ in. mild steel bar. If the molten metal just melts the end of this bar, bringing it to a point, it can be assumed that the temperature is around 1,500° to 1,550° C. If the bar does not quite melt, but evolves sparks, then the temperature is in the lower range of 1,450° to 1,500° C. No metal of the types mentioned should be poured into castings lower than 1,450° C.

In view of the high pouring temperatures entailed, care must be taken to ensure fairly refractory and permeable moulds. The best results are obtained by the use of dry sand moulds, but green sand moulds can be utilised for small castings if necessary. Attention is directed to the moulding sands used, and the author states that the best dry sand for the job is of the more open mixtures as used for the production of iron castings made from naturally bonded or synthetic sand having an A.F.A. permeability number of not less than 80 with a dried compression strength of not less than 50 lb. per sq. in. Good results can also be obtained by making the mould in oil-sand, using four parts of sea sand to one part of red sand as a base.

The methods of moulding several types of valve lids are discussed and illustrated in some detail. In one instance, for example, the author states that very satisfactory results have been obtained in practice by moulding the seat face down in dry sand and casting the boss solid. A large tapered riser is attached for feeding purposes, and the casting is poured through this riser from a runner bush by a number of ⅜ in. jets, arranged circumferentially so that the metal streams do not strike the mould wall. The height of the riser should be greater than the depth of the boss underneath. Direct pouring into the feeding head is the only way of ensuring the hottest metal at this point, and the use of a pouring bush with jet runners minimises the ingress of slag and also has the additional advantage of acting as a " hot-top " which materially assists in keeping the metal in the riser fluid until the casting has solidified. There is, of course, no need to allow the runner bush to retain metal, and pouring can be stopped before the feeding head is full, so that the runner bush empties itself into the casting.

In discussing the influence of design on valve life, reference is made to design of lids incorporating a very long pintle where doubt will exist as to whether any method of moulding will produce a satisfactory casting. In such cases it is worth while taking the matter up with the designer as to whether the pintle cannot be made from wrought bar, and subsequently fitted by mechanical means, or cast into the lid in the foundry. In the past there seems to have been very little effort made to " cast-in " pintles, but it should be quite a practical operation providing the body section is heavy enough to ensure the passage of enough metal to effect welding of the pintle with the body. The pintle can be made from Monel bar, and the end going into the casting should be machined with a series of deep knife-edged parallel grooves to facilitate its union with the molten metal in a similar manner to that employed for a certain type of chaplet. The high pouring temperatures employed for the type of castings under review should promote satisfactory fusion, but if any difficulty is experienced recourse could be made to coating the grooved end of the pintle section with pure tin.

The methods of moulding described do not readily lend themselves to the production of " cast-on " test-bars and the supply of separately cast bars should be adopted. Various moulding methods, which can be adopted for these test-bars are illustrated in the paper. In conclusion, the author emphasises that steam valve lids for marine service are required to stand up to arduous conditions these days, and only the best is good enough. If a casting is not wholly satisfactory, then scrap it without compunction, and on no account attempt to patch it up by welding, nor disguise its solidity by peening or any other means.

British National Specifications for Cast Iron

This paper by J. G. Pearce reviews the position of cast-iron specifications. The establishment in 1928 of the first national specification for general grey-iron castings (B.S.S. 321/1928), with which the original Test-bar Committee of the Institute was actively concerned, was a landmark in the history of cast-iron testing. Among the revolutionary features of this specification were :—

(1) The introduction of the tensile test for use in parallel with the transverse test, previously used almost exclusively.

(2) The adoption of cylindrical test-bars, rendering obsolete the rectangular and square bars previously used, accompanied by the option of machining the transverse bar.

(3) The acceptance of the principle of adjusting size of bar to section of casting represented by it.

(4) The adoption of test-bars cast separately from the casting.

In addition, the specification both actively and passively —that is, both by what it said and by what it did not say— powerfully reinforced the principle that for general purposes iron castings should be specified by their mechanical properties, and that composition should be left to the discretion of the founder.

Experience has confirmed the accuracy of the original basis, which has been extended, and in minor degrees modified. To-day there are six grades of iron covered in two specifications, 321 and 786, ranging from 9 to 26 tons per sq. in. in tension, and five test-bar sizes in place of the original three. As was hoped, the basis of testing has been adopted both in new and in revisions of earlier B.S. Specifications. It has had repercussions abroad. A great deal of experience has now been recorded on the round bar, to be found in British, U.S. and Continental sources. The war has given an enormous impetus to the use of these specifications, both for new products and for cast-iron replacements of other materials. Their existence has been a great advantage to the industry.

In some quarters, a demand for revision has been expressed, to take care of the minor inconsistencies arising from the growth of the specification on a basis of experience and the inevitable compromises of committee working. Attention has been drawn, for example, to the gap between the highest grade in 321 and the lowest in 786 ; to the fact that the transverse strengths do not entirely line up with the tensile strengths, and to the fact that the lowest grade of 786 is not normally accepted as high-duty iron. Such a revision must wait on events, but it may be of interest to foreshadow some directions in which improvement may be made and to furnish a basis for discussion, although pressure of other work under present conditions has prevented this being made as complete as was intended. The points raised concerned the transverse test, deflection, transverse-tensile relationship, influence of size of bar, and separately cast test-bars, all of which are controversial. It is noteworthy in regard to separately cast test-bars that little difficulty has arisen from the use of separately cast test-bars, the metallurgical desirability of which, compared with the cast-on bar, is now accepted. It is noteworthy that one important authority some years ago expressed its willingness, in case of dispute, to accept the identity of test-bar and casting

by an analysis for either silicon or phosphorus. The sensitivity of the analytical method is greater than the difference between the test-bar and casting, unless they were poured from the same metal at the same time. Standard methods of analysis should, of course, be used. As far as the writer is aware, no case has arisen needing to be settled in this way, and the old argument that if the inspector is not present, the bar must be cast-on to ensure identity of bar and casting has lost its force.

Service Experience with the Newer Condenser Tube Alloys

(Continued from page 76).

incoming circulating water. In the case of Admiralty tubes, most failures have been attributed to local pitting and plug type dezincification ; layer type of dezincification usually occurs in tubes that have been in service for many years. In the case of 70/30 copper-nickel tubes, most failures have been attributed to erosion at the inlet ends, steam impingement wearing down the tube wall from the steam side and to localised pitting usually resulting from the presence of a foreign particle.

In order to combat the effects of inlet end impingement attack and still retain the high corrosive-resistant qualities of 70/30 copper-nickel, the Bureau of Ships has developed an ideal plastic condenser tube end protector fabricated from bakelite, neoprene, and combinations of bakelite and neoprene. It was found that the inserts have a long service life and ideally protect the inlet ends of the tubes.

American Foundry Convention

The technical reports and papers presented at the recent annual convention of the American Foundrymen's Association stressed those developments of the industry which are of outstanding importance in the production of castings for the national defence programme. Papers and discussions covered general developments in plant and equipment, foreman training, apprentice training, job evaluation and time study, safety and hygiene, refractories, sand research and foundry cost methods. Each division of the Association (comprising grey iron, steel, malleable, non-ferrous and patternmaking) had its own schedule for the presentation of formal papers and discussion of papers and reports. In all some 37 technical sessions were promoted during the Convention.

Industrial and Export Council

At the invitation of the President of the Board of Trade the Hon. Geoffrey Cunliffe has joined the Industrial and Export Council as a Business Member. He relinquishes his post as Aluminium Controller to the Ministry of Aircraft Production, but will still be available for consultation.

Control of Asbestos

The Order (S.R. & O. 1941, No. 742) also extends the control in respect of asbestos (raw and fibre), and makes minor relaxations in the list of drugs requiring export licences.

Copies of the Order (price 1d.) are available at the Stationery Office.

We have received an informative booklet from the Brookside Metal Co., Ltd., Stanmore, Middlesex, giving particulars of the " Broo-zinc " die and sand-casting alloy. It gives the composition and physical properties of this alloy, together with the results of various tests, information on casting and machining properties, as well as brief reference to applications of the alloy.

The Beta Region of the Gold-Cadmium Alloy System

THIS paper, by Professor E. A. Owen and W. Howard Rees,[*] gives an account of an X-ray investigation of gold-cadmium alloys containing between 38 and 62 atomic per cent. of cadmium, a range of composition that covers the β region of this system shown in the equilibrium diagram as published in the International Critical Tables which represents the results obtained by Saldau[1] from determinations of the electrical conductivities of gold-cadmium alloys.

As a result of the present investigation, however, it was discovered that the β region contains two pure phases, separated by duplex regions from each other and from adjacent pure phases. The pure region at the gold-rich end, designated a_3, which has a rhombohedral structure, extends over a range of composition from 46 to 48·5 atomic per cent. of cadmium at 200° C. and from 41 to 47·5 atomic per cent. at 600° C. ; the pure region at the cadmium-rich end, designated β, is of irregular shape, but at 300° C. it extends from 50·2 to 54·5 atomic per cent. of cadmium. The β phase has a body-centred cubic structure in which the gold and cadmium atoms are in ordered arrangement.

The two new phases, designated a_2 and a_3, which are not shown in previous equilibrium diagrams of the system, and the β phase extends over a much narrower range of composition than was previously believed. Before finally accepting these new boundaries it would be well, in view of the fact that the β phase is found to be unstable at ordinary temperature, to investigate alloys in this region at elevated temperatures ; this demands special technique and will have to be conducted at a later date.

In the β phase the gold and cadmium atoms tend to take up their positions in the two simple cubic lattices which interpenetrate to form the body-centred cubic lattice. The authors state that it was impossible to decide definitely from the spectra taken with alloys in adjacent two-phase regions, on account of the large number of spectral lines which they contain, whether the order found in the pure phase existed when the phase was mixed with the adjacent pure phases. From a careful examination of some of the spectra it was considered there was evidence that this was so, but it is advisable to make more extensive observations before reaching a final conclusion on the point.

The solidus and liquidus lines shown in the diagram[2] follow as nearly as possible the lines included in Olander's diagram. Where any modification is made to accommodate the new phases, this is entirely without experimental evidence to support it, excepting the fact that the present results reveal that a change in these curves is necessary.

Electrolytic Polishing of Steel Specimens

(Continued from page 92).

specimen had been ground to the required fineness was approximately 10 minutes.

In this method of etching, a point of importance to be noted is that the electrolyte (a solution of perchloric acid and acetic anhydride) is violently explosive and must therefore be handled with extreme care. Contamination with alcohol and other organic substances is particularly to be avoided. No attempt should be made to electro-polish bismuth or bismuth alloys or any specimen mounted in organic moulding material. Specimens mounted in bakelite cannot be electro-polished because the electrolyte attacks the bakelite and causes severe staining. Copper strips often used to separate a group of specimens mounted in a steel clamp also cause staining.

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[*] *Jour. Inst. of Metals*, 1941, **67**, pp. 141-151.
[1] P. Saldau, *Internat. Z. Metallographie*, 1915, **7**, 3.
[2] A. Olander, *J. Amer. Chem. Soc.*, 1932, **54**, 3819.

Reviews of Current Literature

Metals and Alloys

This is the fourth edition of a list of metals and alloys which was first published in 1920. In this edition, covering some 3,700 compositions, a complete revision has been made and the details of a considerable number of additional alloys have been added. The alloys covered are regarded as non-ferrous, and are limited to those containing not more than 50% of iron. It is primarily a list of alloys having definite names, either proprietary alloys of which the compositions have been recorded, or those other alloys such as Muntz Metal, Naval Brass, etc., which, although not proprietary, or no longer so, have usually a very definite composition.

In addition to those alloys with definite names, a good many alloys, to which specific names are not attached, have been inserted under their appropriate headings such as Brasses, Bronzes, Cupro-Nickel Alloys, etc., generally under the description of the duty served by the particular alloy. This edition represents a considerable advance on previous editions, and those familiar with its predecessors will find it much more valuable for reference purposes and especially as a guide to the applications of metals and alloys for particular purposes. It is compiled and published by The Louis Cassier Co. Ltd., 18, Loom Lane, Radlett, Herts.

The Spectrochemical Analysis of Metals and Alloys

THE author has had such long experience in the field which the book covers and has an international reputation on the subject that any book by him on spectrochemical analysis will be recognised as authoritative. It is noteworthy, however, that he is dissatisfied with the name and regards the phrase " spectrochemical analysis " as clumsy, and hopes that some genius will coin a more appropriate and labour-saving word which can be applied. In addition to spectrochemical analysis, this method of analysis is referred to as spectrum analysis, spectrographic analysis, and spectrographical analysis, all of which are clumsy, but the writer is inclined to the use of the name of spectrographic analysis as being less misleading than spectrochemical analysis ; however, all terms are now well understood.

Considerable progress has been made, both in this country and elsewhere, in the application of the spectroscope to quantitative determination of impurities in many non-ferrous metals and also in the control of composition of metals and alloys. In a large measure this has been due to persistent work involved in developing a suitable technique, not only in using the spectroscope but in measuring the photographed spectrum obtained. As a means of making a qualitative analysis of an alloy, as a preliminary to chemical analysis, it has long been found advantageous in many cases, and it is much used for this purpose, but progress has been in the direction of using the instrument to estimate the quantities of element present in an alloy with a degree of accuracy sufficient for practical purposes. The results of much work on the subject has certainly encouraged the adoption of the spectroscope, particularly for certain routine applications, and this book will assist the increasing adoption of the instrument.

The author traces the development of spectrochemical analysis from the discovery of the dispersion of light by Newton to the construction of the first spectroscope by Frannhofer in 1817, and subsequently to the spectrochemical analysis investigation of Hartley and Gramont. This historical discussion, together with chapters on the elements of atomic spectrum theory, spectrographs and necessary apparatus, and the microphotometer, are given in the first part. It is the second and main section, however, which is of greater practical value to the metallurgist There are six chapters in this section which deal respec-

tively with methods of exciting emission spectra ; taking spectrograms, measuring wavelengths, and intensifying elements ; technique of spectrochemical analysis ; types of problem to which spectrochemical analysis is applicable ; the practice of spectrochemical analysis of metals and alloys—this chapter covers a wide range of metals and alloys ; and the analysis of substances not in metallic form, including gases. Two appendices are included giving units and definitions, and additional notes ; the book is completed with a comprehensive bibliography, author and subject indices.

In compiling this book the author had in mind teachers and students of metallurgy who wish to acquaint themselves with the scope and nature of spectrochemical analysis as it is carried out in industrial laboratories ; metallurgists already engaged in industry to whom it may fall to introduce the method for routine control or research ; and those who are already engaged in this kind of analysis. The text is ably and concisely written, and is supported by 61 illustrations and 22 tables, and its object has undoubtedly been fulfilled, since this book will be invaluable to metallurgists and students who are seeking full information on the subject of spectrochemical analysis.

By F. Twyman, F.R.S. Published by Charles Griffin & Co. Ltd., 42, Drury Lane, London, W.C.2. Price 21s. net.

Spectrochemical Abstracts

VOL. II., 1938-1939

THIS is the second volume to be published under the above title : the first covered the periods 1933-1935, while the present volume covers the next two years and includes a few important earlier papers and also books published in 1940. Some idea of the work on spectrochemical analysis during this relatively brief period is indicated by the amount of literature devoted to its various aspects ; thus 166 abstracts are given from technical literature which describe or discuss substances analysed and some of the elements determined. These abstracts are numbered consecutively with those of the first volume. The book includes authors and references arranged alphabetically under the authors' names, and in a very convenient form for quick reference.

This book is compiled by Ernest H. S. van Someren, B.Sc., and published by Adam Hilger Ltd., 98, St. Pancras Way, London, N.W.1.